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HOP INVESTIGATIONS

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INTRODUCTION.

This is not a bulletin dealing with the general methods of hop growing. The reader desiring this kind of literature is advised to secure Farmers' Bulletin No. 304 and Circular No. 56, Bureau of Plant Industry, from the United States Department of Agriculture, Washington, D. C. The subject matter here presented embodies the greater part of the results obtained from some experimental work begun about two years ago by the chemical division of this station. The work was carried out under the Adams Act of the United States Government, an act which provides for scientific investigations by the agricultural experiment stations.

Although the greater part of the results reported are easily understood by the average reader, some of them are very technical in their nature, especially the portion dealing with the methods of chemical analysis. This portion is not extensive, however, and it seems best to publish all the results in one bulletin instead of two separate bulletins, one popular for general distribution and the other technical for research workers and technologists.

The work completed has been done along special lines which a thorough study of the literature on the subject and a consideration of local conditions seemed to indicate of most immediate value. The specific points studied naturally fall under six different heads: (1) The fertilizer requirements of the hop plant, (2) methods for the chemical analysis of the hop, (3) the changes in composition of the hop during the ripening period, (4) the effect of kiln drying at 145° Fahr. on the composition of the hop, (5) a comparative study of the composition of Oregon hops, and hops from other localities, and (6) a comparison of commercial and scientific methods of hop valuation.

ACKNOWLEDGMENT: The first part of the work here reported was begun while Professor C. E. Bradley was chief chemist of the station. The writers wish to thank Professor Bradley for proposing the investigation and for his suggestions, interest, and assistance during the early part of its progress.

CHAPTER I

Experiments With Commercial Fertilizers.

In some of the older hop yards of Oregon the hills have a tendency to die out or "miss." This "missing hill" trouble is a serious one in some of the old yards on the bench lands. It also occurs to a limited extent in some of the yards planted on sandy river bottom land. In the yards which the hills have begun to "miss" there is always a decrease in yield.

One of the explanations which have been offered for the cause of the "missing hill," is that the soil has been depleted of its supply of available plant food. In other words, the soil has become impoverished by clean cultivation and the demands of the hop plant. If such an explanation were true, it might be expected that liberal applications of commercial fertilizers would be advantageous.

In the spring of 1910, this department began some fertilizer experiments on the yards of T. A. Livesly at Salem and H. Hirschberg at Independence, Oregon. The Livesly yard was about twenty years old, and although near the river, was on low bench land of a silty type. The Hirschberg yard, also an old one, was on overflow river bottom soil, which was sandy in its nature. Both yards had shown a considerable decrease in yield as compared with former years. Fertilizers containing the different critical plant foods (the plant foods in which a soil may be deficient), nitrogen, phosphorus, potash and lime, were tried separately and in mixtures. The fertilizers were applied March 4 and 5 and were well worked into the soil immediately around the hills. A row of twenty-two hills was tried in each instance. Only every third row was fertilized, thus leaving two rows on each side of the fertilized rows for comparison.

The arrangement of each test plot, together with the amount of fertilizer applied to each twenty-two hills, was as follows:

Rows 1 and 2	Blank.
Row 3	6 lbs. nitrate of soda (rate 245 lbs. per acre).
Rows 4 and 5	Blank.
Row 6	12 lbs. muriate of potash (rate 490 lbs. per a.)
Rows 7 and 8	Blank.
Row 9	6 lbs. acid phosphate (rate 245 lbs per acre).
Rows 10 and 11	Blank
Row 12	6 lbs. nitrate of soda, 12 lbs. muriate of potash, 6 lbs acid phosphate (rate 980 pounds of mixture per acre)
Rows 13 and 14	Blank
Row 15	12 lbs. nitrate of soda (rate 490 lbs. per acre).
Rows 16 and 17	Blank.
Row 18	18 lbs. muriate of potash (rate 735 lbs. per a.)
Rows 19 and 20	Blank.
Row 21	12 lbs. acid phosphate (rate 490 lbs. per acre).
Rows 22 and 23	Blank.
Row 24	12 lbs. nitrate of soda, 18 lbs. muriate of potash, 12 lbs. acid phosphate (rate 1715 pounds of mixture per acre).
Rows 25 and 26	Blank.
Row 27	30 lbs. of lime (rate 1224 lbs. per acre).
Rows 28 and 29	Blank.
Row 30	60 lbs. of lime (rate 2448 lbs. per acre).
Rows 31 and 32	Blank.
Row 33	6 lbs. land plaster (rate 245 lbs. per acre).
Rows 34 and 35	Blank.
Row 36	12 lbs. land plaster (rate 490 lbs. per acre).
Rows 37 and 38	Blank.
Row 39	30 lbs. land plaster (rate 1224 lbs. per acre).
Rows 40 and 41	Blank.

The hop vines were observed carefully at different times during the growing season. The plots were kept well cultivated until the first part of July. At no time during the entire season did it appear that the vines which had been fertilized were doing better than the unfertilized. In only one instance could any benefit whatever be noted; in the plot on the Livesly yard where the twelve pounds of nitrate of soda were applied the vines were a little more thrifty in appearance. Upon gathering the hops from these vines, however, it was found that there was no increase in yield. Considered as a whole, the results were negative.

Prior to the making of the preceding experiment, Professor

C. E. Bradley, former chemist of the Station, tried some fertilizer tests on a hop yard on hill land near Banks, Oregon. The results of these tests were also negative.

During the summer of 1910, several Willamette Valley yards which had been fertilized were visited, and the results of the fertilization carefully observed. Most of these yards had been fertilized with commercial brands of complete fertilizers of guaranteed composition. In no instance where the commercial fertilizers had been used on older yards could any benefit be noted. On one of the hill yards near Forest Grove fish guano, applied to some hops which had just been planted, had an exceedingly beneficial effect. This was due no doubt to the fact that the root system of the young plants was not large and the addition of the fertilizer increased the amount of plant food available for the plant. Older yards close by, and on the same soil upon which this fertilizer had been applied, showed negative results.

Of all the fertilizing materials which have been used in the Willamette Valley, ordinary barn-yard manure seems to give the best results. Reports from every instance where this has been used indicate that it has a very beneficial effect on the growth of the hop. Its effect seems to be out of all proportion to the actual amount of plant food added, and the good results obtained from it are perhaps due to other factors, such as the improvement of the physical condition of the soil, the conservation of moisture, etc. When it is applied in too large quantities, however, it makes the foilage too heavy and the hops too slow in maturing.

The writers realize that the data here presented is limited, and that before definite conclusions can be drawn more extensive experiments should be made, using a great variety of fertilizing materials. This work should be done very thoroughly and carried out through a number of seasons and on different kinds of soil. We are not alone in this opinion. Doctor W. W. Stockberger, of the United States Department of Agriculture, who has been studying hop culture for a number of years, has recently written to us regarding the use of commercial fertilizers on hops, as follows:

"In reply to your recent favor regarding commercial fertilizers for hops, I regret to say that up to the present time I have secured very little exact data on this important subject. Many American hop growers have advised me that they have derived little apparent benefit from the application of commercial fertilizers to hops, while on the other hand, the use of stable manure has been distinctly beneficial.

"European hop growers have apparently had better success with commercial fertilizers. Professor Foss, of Neutomischel, Germany, says that stable manure alone does not increase the yield of hops so much as when it is combined with a commercial fertilizer. Dr. Wagner, of Weihenstephan, Germany, found as a result of four years' experiments that on the average a complete commercial fertilizer gave a much higher yield than stable manure. In view of these divergent results I think we should be careful not to draw radical conclusions from limited experimental data."

Considering our experiments and observations, however, we are led to conclude (1) that the results thus far obtained with some of the ordinary fertilizers indicate that these materials cannot be used profitably in the culture of the hop in the Willamette Valley; (2) that barn-yard manure is the best fertilizer yet found for this purpose; and (3) that the "missing hills" with the consequent decrease in yield in the older yards, is perhaps not due directly to a lack of available plant food, but to other factors.

CHAPTER II

A Comparative Study of Analytical Methods for the Determination of Hard and Total Soft Bitter Resins in the Hop.

Scientific investigations have shown that the hop cone contains three so-called "resins," two of which have a characteristic bitter taste and are known collectively as the "hop bitter" or "bitter principle." These resins are constituents of the lupulin granules of the hop cone, and are distinguished as the "alpha" resin, the "beta" resin and the "gamma" resin. The alpha and beta resins are the soft "bitter" resins, the "bitter principle." When separated from the hop cone, these two resins are found to be definite crystalline, chemical compounds of constant composition. The composition of the alpha resin may be represented by the chemical formula $C_{20} H_{30} O_3$ and the beta resin by the formula $C_{25} H_{36} O_4$. In other words, the two resins are composed of the chemical elements carbon, hydrogen and oxygen, the alpha resin containing 68.52 per cent of carbon, 8.63 per cent of hydrogen, and 22.84 per cent of oxygen, and the beta resin 74.94 per cent of carbon, 9.06 per cent of hydrogen, and 15.99 per cent of oxygen. They are both weak acids (so-called pseudoacids) and are in many ways very similar. They give to the hop its preservative and flavoring qualities. The gamma resin is commonly known as the "hard" resin; it has no definite composition and is tasteless.

The soft bitter resins are of first importance in the consideration of the hop for its commercial uses. During recent years, investigations have shown that *the value of the hop is due mainly to its content of these resins*. In fact, some international authorities have stated that these are the *sole* factors affecting quality.

Because of the great importance of the soft bitter resins, accurate analytical methods for their determination are of first importance. They are a prime requisite to any thorough study of the composition of hops; no exact data concerning the chem-

ical changes taking place in the hop during ripening period (see Chap. IV) or during the drying process (see Chap. III), can be secured without the use of accurate chemical methods for the estimation of hop resins.

At the beginning of our investigations, therefore, a thorough study was made of the hop literature available, in search of correct methods for the determination of the hop resins. It was found that a great variety of results had been obtained by various chemists using different methods of analysis. Much of the data is conflicting and would lead one to suspect that some of the analytical methods used were inaccurate; and as a consequence, in many instances, erroneous results had been obtained. At any rate, no analytical methods for the determination of these resins were found which without further trial gave promise of the accuracy required in the experimental work to be taken up.

It was necessary, then, to make a comparative study of the analytical methods which had been worked out for the determination of the total soft bitter (alpha resin plus beta resin) resins and the "hard" (gamma) resin. In this study, two different methods for the determination of both hard and total soft resins have been given a test: Briant and Meacham's (*Jour. Fed. Inst. Brewing*, 3, 233, 1897) method and Siller's (*Ztg. Untersuch. Nahrung-Genuss.*, 18, 241) method. The original volumetric method of Lintner (*Ztg. Ges. Brauwesen*, 21, 407) and the modified Lintner (*Chem. Ztg.* 32, 1068; O. Neuman, *Wochenschrift fur Braueri*, 1910) method for total soft resins have also been studied. Although the original Lintner method has been shown to be inaccurate, we have included it in this study because we have found from our correspondence that this method, in a few instances, is still employed. A method which has been worked out in this laboratory is given, and the comparative results are reported. We have had good success in the use of this method, and while not claiming originality for the basic principles involved, we believe it overcomes some of the objections to present methods. For convenience, it is here designated as the "Oregon Station method." Not all of the methods for the estimation of hop res-

ins are given, but we believe all have been included that are receiving an extensive use.

METHODS.

In all the methods which have been devised for the determination of hop resins, the separation of the soft resins from the hard resin is dependent upon the ready solubility of the former in petrolic ether, the latter being practically insoluble in this solvent. The extraction of total resins from the hop is effected with ordinary ether.

Briefly stated, the methods compared are as follows:

Briant and Meacham's Method. About four grams of hops are placed in a Soxhlet extractor and extracted for twenty-four hours with petrolic ether (boiling point 50° Centigrade). After extraction is completed, the extraction flask is disconnected from the apparatus and its contents filtered while hot through a small filter paper into a weighed, wide-mouthed flask; the filtrate is then gently evaporated. The final drying operation is completed by placing the flask on its side in a hot water oven, where it is maintained at a temperature slightly above the boiling point of the ether until its weight is constant. The extract thus obtained is the total soft bitter resins in the sample.

The hops left in the extractor from the petrolic ether extraction are next extracted with ordinary ether for twelve hours. The ethereal extract is then filtered into a weighed flask, dried and weighed as in the previous extraction, the residue obtained being estimated as hard resin.

Siller Method (a) Soft Resins. A ten-gram sample of hops which have been ground through a small meat grinder is placed in a Soxhlet extractor and extracted with petrolic ether (boiling point 30 to 40° C.) for eight to ten hours. The petrolic ether extract is then evaporated *in vacuo* on a water bath at 40° C. until all of the solvent is removed. The residue is then taken up with methyl alcohol to separate the wax present, filtered and made to 100 cc. volume. An aliquot portion of 10 cc. (equal to one gram of hops) is placed in a weighed flask, and the alcohol is then completely evaporated in a drying oven at 80° C., the evaporation requiring

four to five hours. The residue obtained is estimated as total soft bitter resins.

(b) *Total Resins.* A ten-gram sample of ground hops is placed in a Soxhlet extractor and extracted eight to ten hours with ordinary ether. The ethereal extract is then evaporated *in vacuo* at 40° C. until all of the ether is removed. The residue obtained is taken up with the methyl alcohol to separate the wax, filtered and the filtrate made to 100 cc. volume. A 10 cc. aliquot (equivalent to one gram of hops) is placed in a weighed flask, evaporated and weighed in the manner used in the determination of total soft resins, the residue obtained representing the total resins in one gram of hops.

The hard resin is estimated by the difference between the amounts of total resins and soft resins.

Lintner's Volumetric Method for Soft Resins. This method is based upon the fact that the two bitter substances commonly called soft resins react in solution as monobasic acids with alkalies.

A ten-gram sample of hops is introduced into a 500 cc. flask having also a mark at 505 cc.; 350 cc. of light petroleic ether (boiling point 30 to 50° C.) are added and the flask attached to a reflux condenser. The flask is then heated on a water bath and the extraction continued for eight hours. When cooled to 17.5 degrees C., the liquid is made up to the 505 cc. mark, well shaken and then filtered. One hundred cc. of the filtrate are mixed with 80 cc. of alcohol, ten drops of phenolphthalein solution (1:100) added, and then titrated with a tenth-normal solution of potassium hydroxide until the red tint just appears. A blank experiment is made to ascertain the amount of potassium hydroxide neutralized by the mixture of alcohol and petroleic ether. The number of cc. required for the titration multiplied by the factor 0.04 (the molecular weight of the bitter substance taken as 400) represents the amount of soft resins in the aliquot.

Modified Lintner Method for Soft Resins. The determination is carried out in the same manner as in the original Lintner method, except that the hops are ground previous to the extraction.

Oregon Station Method. Ten grams of hops are placed in a Soxhlet extractor and extracted with ether for eight to ten hours. The ethereal extract thus obtained is filtered and the filtrate made to 200 cc. volume.

(a) *Total Resins.* One hundred cc. of the ether solution (equivalent to five grams of hops) are placed in a 250 cc. Erlenmeyer flask and nearly all of the ether removed by distillation on a water bath at about 40° C. The last portion of the ether is completely removed by drying in a vacuum desiccator at room temperature. The residue remaining is then taken up with alcohol to free the wax, filtered and the filtrate made to 100 cc. volume. A 20 cc. aliquot (equivalent to one gram of hops) is transferred to a weighed beaker and the alcohol removed by evaporation in a vacuum oven at 50° C. to constant weight. The residue thus obtained is the total resins in one gram of hops.

(b) *Total Soft Resins.* The remaining 100 cc. of the original ether extract are transferred to a 200 cc. Erlenmeyer flask and the ether nearly removed by distillation at low temperature, the last portion being removed by evaporation in a vacuum desiccator at room temperature. The residue is taken up with about 100 cc. of petrolic ether (boiling point 40 to 45° C.). The residue is worked up in the solvent with a glass rod and then let stand a short time to effect the complete solution of the soft resins in the solvent. The hard resin is then removed by filtration. The petrolic ether is removed from the filtrate in the same manner as the ether in the first part of the determination. The residue is taken up with alcohol to remove wax, filtered and the filtrate made to 100 cc. volume. An aliquot of 20 cc. (equivalent to one gram of hops) is transferred to a weighed beaker and evaporated and weighed as under the determination of total resins.

The hard resin is estimated by difference between the total resins and soft resins.

COMPARISON OF THE METHODS.

Five samples of Oregon hops of the 1910 crop were analyzed, using each of the different methods given above. Sample No. 1 was an air-dried sample and Nos. 2 to 5 were com-

mercial samples which had been kiln-dried. In each instance the extraneous matter, such as leaves and stems, was separated, only the whole unbroken cones being used for the determinations. The results of the analyses are given in Table I.

The table shows a wide variation in the results obtained by the different methods. Siller's gives extremely high results for soft resins, while Briant and Meacham's and the original Lintner methods show very low results. The amount of soft resins obtained by Lintner's modified method and the Oregon Station method agree fairly well. Briant and Meacham's method shows very high results for hard resins, while Siller's and the Oregon Station methods give much lower amounts.

The low results for soft resins obtained by the Briant method and the original Lintner method are due to the fact that the extraction of the soft resins is not complete. The lupulin granules of the hop cone must be well broken up before the soft bitter resins can be completely extracted with petrolic ether. Siller (*Loc. cit.*) has already pointed out this fact and has suggested the grinding of the hop previous to the extraction as a means of overcoming this defect. Grinding by means of a meat grinder or with sand in an ordinary mortar has been found satisfactory for the preparation of the samples for extraction. When the meat grinder is used, the sample is taken after the material has been ground.

The high percentage of hard resin secured by Briant and Meacham's method is due to the presence of soft resins left from incomplete extraction with petrolic ether. Another slight error in this method is caused by the failure to separate the wax; but this is not great, the amount of wax present amounting to only 0.25 to 0.45 per cent.

The extremely high results for soft resins given by Siller's method have been found to be due to the extraction of material from the ground hop seed. The method was worked out, no doubt, with seedless continental hops, and consequently this point did not receive consideration. It has been found in this laboratory that although the unground seed gives no appreciable extract with petrolic ether or ordinary ether, the ground seed yields a considerable amount. Seeds taken from four different samples of Oregon hops were ground and extracted

TABLE I.—THE RESIN CONTENT OF OREGON HOPS BY DIFFERENT METHODS.

Method.	Sample 1.			Sample 2.			Sample 3.			Sample 4.			Sample 5.		
	Hard resin, per cent.	Soft resin, per cent.	Total resin, per cent.	Hard resin, per cent.	Soft resin, per cent.	Total resin, per cent.	Hard resin, per cent.	Soft resin, per cent.	Total resin, per cent.	Hard resin, per cent.	Soft resin, per cent.	Total resin, per cent.	Hard resin, per cent.	Soft resin, per cent.	Total resin, per cent.
Briant & Meacham's	8.00	9.09	17.09	7.95	9.14	17.09	11.54	8.84	20.38	11.37	8.59	19.96	7.54	8.68	16.22
Siller's	2.89	20.07	22.96	2.76	16.50	19.26	2.52	21.49	24.01	1.93	20.96	22.89	1.33	17.01	18.34
Oregon Station	1.97	16.78	18.75	1.29	15.79	17.08	1.52	18.50	20.02	1.79	17.29	19.08	1.89	13.73	15.62
Lintner's original	8.88	8.00	5.20	6.80	6.40
Lintner's modified	16.60	16.00	19.32	18.00	13.20

in Soxhlet extractors with ether and petrolic ether. The results are given in Table II.

TABLE II.—EXTRACTIVE MATTER IN GROUND HOP SEEDS.

	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
	%	%	%	%
Petrolic ether extract.....	24.05	24.72	27.30	20.36
Ether extract	26.52	26.04	21.70	29.64

There is approximately 25 per cent of the ground seed which is soluble in each of these solvents. This would permit a large error in the determination of soft resins in seeded hops by Siller's method, especially in Pacific Coast hops, where the amount of seeds is high, ranging from 11 to 20 per cent.

The estimation of hard resin by taking the difference between the amounts of total and soft resins obtained from separate samples is often inaccurate because of the wide variation in the resin content of the samples. Duplicate ten-gram samples of the same hops sometimes show a variation of $1\frac{1}{2}$ per cent in the amount of total resins where the total resin content is only 17 per cent. A difference of $\frac{1}{2}$ to $\frac{3}{4}$ per cent is common. By the following experiment this is shown to be due to the wide variation in the resin content of the cones themselves. Six cones of different sizes were selected from each of three different commercial samples, their weight taken, and the amount of total resin in each cone estimated by extracting with ether and drying to constant weight *in vacuo* at 50° C. The results are tabulated in Table III.

The differences between the maximum and minimum percentages of total resin in the cones from each of the samples are 3.87, 3.82, and 6.88 per cent, respectively. The most notable difference is in cones II and III of sample No. 3, where two cones of practically the same weight differ 6.88 per cent. It is evident from these results that samples of at least ten grams weight must be used for the determination of resins, and where accurate results are desired it has been found advisable to make triplicate determinations. *The determination of hard resin, furthermore, should be made on the same identical sample as used for the determination of the soft bitter resins.*

Lintner's modified volumetric method has been found to

TABLE III.—TOTAL RESINS IN INDIVIDUAL HOP CONES.

Sample	Cone I		Cone II		Cone III		Cone IV		Cone V		Cone VI		Max. per cent total resin.	Min. per cent total resin.	Average per cent total resin.
	Wt. of cone in grams.	Per cent total resin.	Wt. of cone in grams.	Per cent total resin.	Wt. of cone in grams.	Per cent total resin.	Wt. of cone in grams.	Per cent total resin.	Wt. of cone in grams.	Per cent total resin.	Wt. of cone in grams.	Per cent total resin.			
1	0.2912	20.74	0.2753	21.57	0.2708	18.35	0.1800	18.88	0.1622	19.05	0.1322	17.70	21.57	17.70	19.38
2	0.2513	18.74	0.3105	20.03	0.3410	18.59	0.2088	22.41	0.1493	21.43	0.1870	20.59	22.41	18.59	20.29
3	0.4943	20.00	0.3075	23.22	0.3035	16.34	0.3630	18.07	0.3335	19.88	0.2064	18.12	23.22	16.34	19.27

give fairly good results. We believe it to be the best available rapid method for the estimation of soft resins suitable for commercial use. Gravimetric and volumetric determinations made on aliquots from the same solution of soft resins show that the volumetric method does not always agree with the gravimetric, often giving results which are somewhat higher. The comparative results of a number of determinations made in this manner from different samples of hops are as follows:

Soft resins, Oregon Station gravimetric method. %	Soft resins, Lintner's volumetric method. %
17.29	17.30
17.75	18.20
14.44	15.00
16.45	17.70
16.64	17.00
15.52	16.70
16.13	16.00
15.58	16.20

The slightly higher results given by the volumetric determinations are perhaps due to the use of the higher of the molecular weights of the different soft bitter resins for making the calculations.

Drying the resins at as high a temperature as 80° C. is open to objection for two reasons: First, the resins turn brown at this temperature and undoubtedly change somewhat in composition; second, a constant weight cannot be obtained. When the resins are dried *in vacuo*, there is no evidence of much change in composition, and when completely dried there is practically no change in weight.

Great care should be taken in securing petrolic ether of suitable quality for the extraction of the soft resins. The practice in this laboratory is to make two distillations, starting with the commercial product sold by dealers (boiling point 40 to 60° C.) and each time taking the fraction, distilling over under 45° C.

CHAPTER III.

The Effect of Kiln-Drying at 145° Fahr. on the Composition of the Hop.

The proper temperature to be used in the kiln-drying of hops is still a matter of dispute. In the different parts of the world, we find temperatures recommended from 70 to 150° Fahr., the best authorities being widely at variance on the question. It is held that during the kiln-drying process at the higher temperatures a portion of the soft bitter resins, (see first part of Chap. II), which give to the hop the major part of its real commercial value, are changed to a hard worthless resin, thereby causing a deterioration of quality. Remy (Chapman, "The Hop and Its Constituents," page 84), a German chemist, tried certain experiments as to the influence of kiln-drying on hops, his results showing that a considerable portion of the soft, bitter resin present in the fresh hop is converted into hard resin. The exact temperature at which these experiments were carried out, however, is not given. Gross (E. Gross, "Hops," page 236), an English authority, writes as follows:

"Greater heat than 68 to 95° Fahr. must not be used or the value of the hops will be reduced, and for this reason the practice adopted; e. g., in America, of drying at 140° Fahr., cannot be recommended as worthy of imitation."

Stockberger (address before American Brewing Institute, 1907) says:

"It is quite generally conceded that the so-called soft resin of the hop alone is valuable, the hard resin being worthless for commercial purposes. Yet the average grower knows nothing of these resins and frequently contrives to dry his hops at a temperature so high that a portion of the essential oil (the volatile oil which gives the hop its aroma) is volatilized and a considerable quantity of valuable soft bitter resin is oxidized and converted into the hard, worthless form. In a series of recent experiments in the field, it has been shown conclusively

that, within limits, the ratio of hard to soft resins varies directly with the temperature used in drying the hops."

So far as the writers know, the results of the experiments mentioned have never been published. Stockberger (Farmers' Bulletin No. 304, U. S. Dept. of Agr., page 24) also states:

"The best temperature for drying is yet to be determined, but every consideration indicates that it should be much lower than that commonly employed, probably between 100° and 140° Fahr."

To the hop growers of the Pacific Coast the proper temperature to be used in kiln-drying is of vital importance. On account of the large size of many of the yards, in some cases amounting to hundreds of acres, the drying must be accomplished in a short time in order to handle the crop. Drying for several days at the low temperature of 70 to 90° Fahr., as is done in some of the European countries where the yards are small, cannot be employed without a practically prohibitory increase in the expense of drying. At the present time, the majority of the hop-growers of Oregon are using a temperature not exceeding 145° Fahr.

Recent investigations made in this laboratory (see Chap. II) have shown that the analytical methods which have been commonly used for the analysis of the hop are unreliable. The methods for the determination of the total soft bitter resins and hard resin have been found to be very faulty. Since unreliable methods of analysis were evidently used for the examination of the hops in the kiln-drying experiments which have been reported, it was deemed advisable to repeat, in a limited way, some of the work which had been done on the effect of kiln-drying on the composition of the hop, especially the effect of a temperature of 145° Fahr.

Samples were taken about the middle of September, 1910, at five different yards, and in September 1911, from two yards. Just as the hops, which has been picked in the usual manner, were being placed on the kiln, a lot of hops, amounting to approximately 100 lbs. of fresh hops, was well mixed; a sample taken, and the exact spot in the kiln from which it was taken was carefully marked. This sample taken previous to kiln-drying was spread out and air-dried in the shade at

the ordinary room temperature. After the hops had been dried on the kiln, a second sample was taken from the identical spot where the first sample had been taken, this second sample representing the hops after kiln-drying. The depth of the layer of hops on the kiln floor ranged from 22 to 30 inches, and the length of time required for drying varied from 18 to 24 hours. The drying was continued in every instance until the stems or cores of the cones were well shriveled, yet still soft and pliable, except in the case of sample 5a where the drying was continued until the stems or cores were somewhat brittle and easily broken. The kiln-dried samples were "sulfured" to the extent of about one-half lb. of sulphur per box of fresh hops (50 lbs.) Great care was taken in handling the samples to avoid any loss due to the breaking of the cones and the sifting out of the lupulin. The hops were all grown on sandy soil along the Willamette river with the exception of samples 4a and 4b, which were grown on hill land.

The kiln-dryers used at the different yards, with one exception, were ordinary "stove kilns" and were representative of those in common use. Samples 3a and 3b were dried on an "air blast" kiln in which air that had been passed over heated steam pipes was forced up through the hops from below by means of a "blast fan."

The temperature used in each instance ranged from 120 to 145° Fahr. The drying was begun at the lower temperature and then gradually raised to 145°, at which temperature it was held as nearly as possible until the hops were dried. The temperature was taken with thermometers which were kept just under the floor of the kiln and at that portion of the kiln where the temperature was highest.

In making the analytical determinations, the methods which have been worked out in this laboratory (see Chap. II) for the determination of hard resin and total soft bitter resins, were employed. The separation of the two soft bitter resins, the alpha and beta (see first part Chap. II) was carried out according to the method outlined by Siller, the German chemist, (*Ztg. Untersuch. Nahrung-Genuss.*, 18, 241). Chapman's method (*Jour. of Inst. of Brewing*, 13, 646, 1907)

was used for the determination of tannin, one of the constituents of the hop cone which may be of value. Moisture was estimated by drying *in vacuo* over sulfuric acid at room temperature. The determination of wax (the hop contains a white, tasteless wax) was made, incident to securing the solutions necessary for the determination of the total resins. The extract obtained by extracting the hops with ether was taken up, after the evaporation of the ether, with alcohol; and the wax, which is insoluble in this solvent, was collected on a weighed filter, thoroughly washed with alcohol, dried at room temperature, and weighed. Owing to the presence of but a small amount of volatile oil (the oil which gives the hop its aroma) and the consequent difficulty of making a quantitative estimation, the determination of this constituent was omitted, and only the physical examination made for aroma. In making the analysis, whole, unbroken hop cones were used.

The results of the analyses are given in Table IV. In order to afford an accurate means of comparison, the amounts of wax, tannin, and the different resins have been calculated to the dry matter, thus eliminating any variation in composition which might be due to the varying moisture content of the different samples.

The results indicate that there was little if any change in the composition of the hops during the kiln-drying process. It will be noted that excepting samples 2a and 2b, the amount of hard resin is slightly greater in the air-dried samples, a result which may be due to variation in different samples. The contention of some authorities that the bitter resins change greatly when hops are dried at as high a temperature as 145° Fahr., is not borne out by these results. There was evidently little if any change in the amounts of tannin and wax, considering the possible variation in separate samples. A physical examination showed that the difference in the aroma of the air-dried and the kiln-dried samples was hardly perceptible, different judges varying somewhat in their opinions; this result perhaps indicates that only a small quantity of the volatile oil had been lost during the drying process.

TABLE IV.—COMPOSITION OF HOPS, AIR-DRIED AT ROOM TEMPERATURE AND KILN-DRIED AT 145° FAHR.

Description of Sample.		Composition of dry matter. Percentages.							
		Moisture.	Total resins.	Total soft bitter resins.	Hard resin. (gamma)	Beta resin.	Soft resins. Alpha resin.	Tannin.	Wax.
No.	1910 crop.								
1a	Kiln-dried from yard of T. A. Livesly, Salem, Ore..	5.14	20.11	18.22	1.89	11.18	7.04	2.50	0.31
1b	Air-dried, corresponding to 1a.....	6.42	21.09	19.02	2.07	11.53	7.49	2.55	0.26
2a	Kiln-dried, from yard of H. Hirschberg, Independence, Ore.	4.33	20.92	19.32	1.60	12.02	7.30	2.31	0.44
2b	Air-dried, corresponding to 2a.....	4.65	20.27	18.72	1.55	12.84	5.88	1.98	0.49
3a	Kiln-dried, from yard of E. Clemens Horst, Independence, Ore.	4.41	19.33	18.56	0.77	12.98	5.58	1.83	0.48
3b	Air-dried, corresponding to 3a.....	5.72	19.82	18.84	0.98	12.50	6.34	2.42	0.43
4a	Kiln-dried, from the yard of F. S. Bradley, Banks, Ore.	5.44	17.37	16.35	1.02	11.73	5.64	2.13	0.40
4b	Air-dried, corresponding to 4a.....	4.75	16.51	15.16	1.35	10.51	6.00	1.97	0.39
5a	Kiln-dried, from yard of Krebs Bros., Independence, Ore.	5.60	19.40	17.62	1.78	12.12	5.50	2.36	0.47
5b	Air-dried, corresponding to 5a.....	4.80	19.36	17.27	2.09	11.11	6.16	2.60	0.47
1911 crop.									
6a	Kiln-dried, from yard of H. Hirschberg, Independence, Ore.	5.60	18.08	17.57	1.51	11.73	5.84	3.60	0.45
6b	Air-dried, corresponding to 6a.....	4.85	19.45	17.49	1.96	11.06	6.43	3.64	0.45
7a	Kiln-dried, from yard of E. Clemens Horst, Independence, Ore.	5.85	20.59	19.17	1.42	13.59	5.58	2.76	0.44
7b	Air-dried, corresponding to 7a.....	7.00	20.62	19.00	1.62	13.53	5.47	3.14	0.44

CHAPTER IV.

The Ripening of Hops.

The changes which take place in the chemical composition of the hop cone during the ripening period are of interest both from the scientific and the technical standpoint. Although the composition of the "bitter principles" of the hop has been known for a long time, the chemical constitution of these principles is a perplexing subject which has in recent times engaged the attention of a number of investigators. From their studies, it appears that some of the constituents of the hop cone are closely related in chemical composition, and it is quite possible that changes take place during the ripening period in which one constituent passes over into the form of another. If this does occur, a study of the composition of the hop cone at different stages of ripeness might be valuable in throwing light on the chemical constitution of the different bitter principles.

From the technical standpoint, it is important that hops should be picked at the degree of ripeness when they possess the maximum commercial value. Recent investigations show that the major part of the actual value of hops, in their industrial uses, lies in the content of soft bitter resins, and hence the amount of these constituents in the hop cone at different stages of ripeness is of prime importance. At present, many of the consumers of hops, regardless of their intrinsic value, insist that they shall be picked somewhat green, while others prefer to have the cones fully ripened. As a result, the hop growers who desire to produce a product of high quality are at a loss to know just when to gather their hops.

In August, 1910, a study was begun at this laboratory of the composition of the hop cone at different stages of the ripening period. The samples were gathered approximately five days apart, the first being picked August 11, the last Sep-

tember 26, and all taken from the yard of the Seavy Hop Company, near Corvallis, Oregon. In collecting, representative cones of various sizes were taken from the upper and outer portion of the vines, an area which was well exposed to the sun. On August 11 two samples were secured, one being of the smaller and the other of the larger and more fully developed cones.

Very soon after the samples were gathered, they were spread out and allowed to dry in the shade at room temperature. When the drying operation was complete, the hops were bagged, great care being taken not to crush the cones and to avoid loss of the lupulin through sifting.

The analytical determinations were made by the same methods that were used in the work reported in Chapter III.

Owing to the presence of only an exceedingly small amount of volatile oil, the oil which gives the hop its aroma, and the consequent difficulty of making a quantitative estimation, the determination of this constituent was omitted.

The results of the analyses are given in table No. V. In order to afford an accurate comparison, the amounts of wax, tannin, and the different resins have been calculated to dry matter.

The results show that there is a continuous increase in the amount of soft bitter resins throughout the ripening period. The riper the hop, the richer it is in these substances, and therefore if high soft bitter resin content is a criterion of industrial value, the fully ripened hop is much to be preferred. The ratio of the amount of alpha bitter resin to the amount of beta bitter resin, is of interest. On August 11, the ratio was 1:3.48, while on September 26, it was 1:1.30. Between the first picking and the last, the amount of alpha bitter resin increased 450.5 per cent, while the beta bitter resin increased but 167.8 per cent. There seems to be no marked change during the ripening period in the amount of "hard" gamma resin, wax, and tannin. From the analytical data, there is also no evidence that one constituent changes to the form of another during the process of ripening.

TABLE V.—COMPOSITION OF HOP CONES AT DIFFERENT STAGES OF RIPENING

Sample No.	Date of picking.	Moisture, matter, percentages		Composition of Dry Matter (Percentages).						
		Dry matter, percentages	Wax.	Total resins.	Total soft bitter resins.	Alpha resin.	Beta resin.	Gamma resin.	Tannin.	
1	Aug. 11 (cones smaller size) . .	8.07	91.93	0.52	10.39	8.44	1.88	6.56	1.95	3.48
2	Aug. 11 (cones larger size) . . .	7.32	92.68	0.57	12.20	10.76	2.74	8.02	1.44	2.92
3	Aug. 16	7.71	92.29	0.37	14.07	12.56	3.53	9.03	1.51	2.98
4	Aug. 21	10.67	89.33	0.55	15.00	13.76	3.84	9.92	1.24	2.59
5	Aug. 26	10.12	89.88	0.34	16.24	14.51	3.92	10.59	1.73	2.88
6	Aug. 31	9.31	90.69	0.46	16.48	15.17	4.82	10.35	1.31	3.06
7	Sept. 5	8.60	91.40	0.35	18.39	16.79	6.27	10.52	1.60	2.81
8	Sept. 11	9.42	90.58	0.32	20.48	18.24	7.07	11.17	2.24	3.36
9	Sept. 19	8.87	91.13	0.38	20.57	18.41	8.47	9.94	2.16	3.28
10	Sept. 26	7.30	92.70	0.33	20.67	19.41	8.40	11.01	1.26	2.76

CHAPTER V.

A Comparison of the Composition of Hops From Different Localities.

In the markets, hops grown in different parts of the world sell for different prices. In this country New York hops usually sell at a higher figure than Pacific Coast hops. In the autumn of 1911, while Oregon hops were selling for 40 to 45 cents a pound, New York hops sold for 55 cents a pound, and the Saaz hops imported from Europe sold for more than \$1.00 a pound.

Upon observing such a condition as this, one is naturally led to ask: Why all this difference in price? Is the actual composition of hops from one locality so widely different from those of another locality as to make them so much greater in value? Does the climatic condition of different countries so vastly affect the actual value of hops?

The writers tried putting such questions as these to men who had been long engaged in hop growing and buying. In response, various and often very conflicting answers were received. The answers obtained from consumers of hops were quite as much at variance. In fact, out of all the answers received to our questions there were not two that exactly agreed. The data obtained would not permit of any definite conclusion, except that people of long experience in the commercial valuation of hops were widely at variance, and no doubt, in many instances, governed by prejudice.

Consequently, in the autumn of 1911 a chemical study of hops from various localities was begun, the object of the study being to ascertain what differences there are in the composition of hops grown in different localities. The samples of Oregon hops were selected by chemists of the station chemical laboratory and were representative. Doctor Alfred C. Chapman, a British chemist who has carried on extensive hop investigations, selected the English samples. We are indebted to Mr. Paul

Weidner, Sr., an experienced and very reliable hop dealer of Detroit, Michigan, for the samples of Washington (state) hops and also the two samples of Saaz hops. Mr. E. Clemens Horst, who grows hops extensively in the state of California, secured the samples of Californians. At the suggestion of the Director of the New York Agricultural Experiment Station (at Geneva, N. Y.) Mr. E. J. Conger of Waterville, New York, was employed to select samples from that state. Doctor A. J. Lehedler of the Pabst Brewing Company, at Milwaukee, selected the sample of Wisconsin. All the samples were as representative as could be secured in this way from the different localities from which they were chosen.

The samples were taken soon after the hop harvest and were analyzed within a few weeks after reaching the laboratory. Meanwhile, they were carefully stored in a cold, dry room to prevent any marked changes in composition from taking place.

The analytical determinations were made according to the methods employed in accomplishing the work reported in Chapter III, except that the cones were not separated from other extraneous matter (leaves, stems etc.) before making the analyses, so that analytical data reported represent the composition of the entire sample. Determinations of the amounts of seeds and extraneous matter were also made.

Other analyses (except in the case of the Wisconsin) than those reported in table VI have been made, but the general relationships were about the same as in those here recorded and the analytical data are omitted to economize space.

TABLE VI.
COMPOSITION OF HOPS GROWN IN DIFFERENT LOCALITIES.

Name of Locality	Moisture	Total Resin	Total Soft Bitter Resin	Hard (Gamma) Resin	Beta Resin	Alpha Resin	Wax	Tannin	Seeds	Leaves and Stems
	%	%	%	%	%	%	%	%	%	%
Washington (State)	3.90	17.55	15.64	1.91	14.85	0.79	0.37	2.02	4.86	5.0
New York No. 1	2.40	14.20	12.81	1.39	8.92	3.89	0.60	1.30	2.50	15.4
New York No. 2	3.10	13.89	12.59	1.30	8.91	3.68	0.68	1.95	2.34	15.0
New York No. 3	4.10	18.51	16.61	1.90	13.81	2.80	0.71	3.06	0.06	9.0
New York No. 4	4.90	16.06	14.20	1.86	11.01	3.19	0.72	2.73	1.84	18.6
California No. 1	3.40	17.31	15.08	2.23	11.61	3.92	0.48	2.04	14.75	3.8
California No. 2	3.70	17.10	15.72	1.38	11.65	4.07	0.52	2.52	18.35	8.8
California No. 3	5.10	12.29	10.79	2.32	4.43	5.54	0.40	1.52	8.38	9.0
California No. 3	5.70	15.76	14.10	1.66	9.14	4.96	0.33	1.40	7.55	13.5
Wisconsin	4.00	15.82	8.68	7.14	7.93	0.75	not determined	2.40	0.22	1.8
England (Worcester)	2.50	12.21	9.97	2.24	6.60	3.37	0.50	1.16	9.55	1.2
England (East Kent)	2.50	11.70	10.51	1.19	7.30	3.21	0.47	1.58	7.90	0.9
England (Sussex)	4.10	12.70	10.35	2.35	6.05	4.27	0.44	2.22	6.15	0.6
England (Farnham)	4.80	12.34	11.06	1.28	6.65	4.41	0.39	1.66	12.50	0.0
Oregon No. 1	6.30	18.35	16.75	1.60	10.56	6.19	0.33	1.67	11.50	7.6
Oregon No. 2	9.20	18.12	16.54	1.58	10.36	6.11	0.37	2.64	11.17	7.2
Oregon No. 3	8.87	18.57	16.57	2.00	8.27	8.30	0.37	2.97	13.56	6.2
Oregon No. 4	6.80	19.80	17.62	2.18	9.48	8.14	0.41	1.99	1.42	4.0
Saaz No. 1	6.50	16.25	14.19	2.06	7.20	6.99	0.54	not determined	none	none
Saaz No. 2	8.20	13.75	12.60	1.15	7.62	4.98	0.45	not determined	none	none

It will be noted that there is a somewhat large variation in the amount of moisture in the samples. This is perhaps due to the fact that some of the samples were stored in our dry store room a little longer than others and dried out somewhat. Generally speaking, we have found the amount of moisture in hops not to vary widely, but to be between 6 and 10 per cent.

The results show that the genuine Saaz hops have no seeds. The amount of seeds in the New Yorks and Wisconsin is not large. In the case of the English samples the range is from 6 to 12 per cent. The samples of Pacific Coast hops contained from 5 to 18.35 per cent. Our examinations of samples of Oregon hops other than the samples here reported, show a high percentage of seeds.

The amount of extraneous matter found gives an indication of the care taken in picking the hops in different localities. For example, the Saaz samples were free from leaves and stems and the English and Wisconsin samples contained less than 2 per cent. These results indicate that great care is taken in gathering the hops in these localities. In the New Yorks the percentage of extraneous matter varies from 9 to 18.6 per cent. Evidently, these hops had been picked in a very careless manner, since some of them contain more leaves and stems than any other samples we have examined. The amount of extraneous matter in the Pacific Coast hops varies from 3.8 to 13.5 per cent. Other examinations made of our Coast hops show wide differences in the amount of foreign matter in the product put out by different growers. We believe that the percentage of foreign matter is a question which must receive much consideration in the correct valuation of hops for commercial use.

The content of soft bitter resins in the different samples

is perhaps the most interesting of the results obtained, because of the great importance of these constituents. The Saaz hops, which demand such high prices in our markets, are somewhat lower in content of soft bitter resin than either the New Yorks or Pacific Coast hops. The English samples were about the same or a little lower in resin content than the Saaz samples. The Pacific Coasts as a rule have a higher percentage of soft resins than the New Yorks, English or even Saaz. These results, with others which we have obtained throughout the entire series of investigations, lead us to believe *that the Oregon grown hops have as great if not greater content of soft bitter resins than hops grown in any other part of the World.* The sample of Wisconsin contained a high percentage of the hard worthless resin. Owing to the fact, however, that only a very small amount of hops is grown in Wisconsin, the writers have not been able to examine other samples to find out if this is generally true of hops from that state.

The variation in the amount of wax is from 0.33 to 0.71 per cent. The content of tannin seems to vary widely even in samples from the same locality. These variations in the amounts of tannin and wax, however, are perhaps of little significance, since the wax is of no value and the tannin is perhaps of only minor value.

On the whole, the results indicate that hops which are now holding a superior position in our markets are, as a matter of fact, inferior in composition compared with other hops which are rated lower commercially. We are led to believe, therefore, that much prejudice prevails regarding the so-called superior value of hops from certain localities in Europe; we have not found any definite facts, at least, to show that they are so much superior in value.

ON STANDARDS OF HOP VALUATION.

At the present time practically all of the hops bought and sold in this country are judged wholly upon the basis of an empirical physical examination. The points considered vary with different judges. Those usually considered most important are: aroma, quantity of lupulin, oiliness, stickiness

or "richness," degree of ripeness, extraneous matter (leaves, stems, etc.), curing, freedom from mould and insects, size of cones, degree of "sulphuring," and care in handling.

The presence of much leaves and stems, mould, insects, broken cones, a scant amount of lupulin and an "off" or "sour" smell, which are generally considered detrimental to the quality of hops are determined simply by inspection. The significance that certain characteristics, such as size of cones, aroma, amount of seeds, "sulphuring," etc., have in determining quality, depends entirely upon the individual judge. Obviously there is, at present no definite standard. The quality is determined by the impressions made by the hop upon the senses of sight, smell, and touch, and not by any definite quantitative estimation of the constituents. At best, the decision of a buyer or consumer is not a definite matter, but simply an opinion that differs widely with different individuals.

Such factors as the amount of lupulin, foreign matter (leaves, stems, etc.), are not estimated by making any exact determinations. What one judge, by mere inspection of a sample, will call "cleanly" picked, another will call "medium," or even "dirty" picked. When asked to state the percent of extraneous matter, the ordinary judge is invariably at a loss to make any definite statement. The same is true regarding the determination of the amount of lupuline, one of the most valuable constituents of the hop, because it contains nearly all of the soft bitter resins. The judgment is based wholly upon looks, and not upon any definite quantitative measurement.

The amount of seeds permissible is a factor upon which there is much difference of opinion. Some maintain that the seeds impart an "off" flavor to the products in which hops are used. Again there are others who hold that the presence of seeds is no detriment, and consequently that "seeded" hops are quite as good as "seedless" hops. Generally speaking, hops containing a large amount of seeds also contain a good quantity of lupuline and soft bitter resins. Salmon and Amos of the Southeastern Agricultural College, Wye, England, have shown that seeded hops not only produce a greater total yield than seedless hops, but also a greater yield per acre of soft

bitter resins. The evidence at hand indicates that the growing of seeded instead of seedless hops, is a distinct advantage to the hop growers, because of the greater yield obtained. So far as the writers can learn, there is no quantitative scientific data available to show that the presence of seeds in hops is actually undesirable.

At present, much importance is attached to the aroma. With many it is the ultimate test of quality. Yet aroma, as a matter of fact, can give no very accurate information as to intrinsic value. It is due to the most volatile parts of the essential oil of the hop; and since in commercial use hops are boiled with other materials, it is highly probable that nearly all, if not all, of the essential oil is volatilized, driven off, and lost during the process. Furthermore, Chapman, an English chemist, who has studied the volatile hop oil more widely perhaps than any other man, has found that samples of hop oil obtained from hops grown in different countries do not differ widely in chemical composition, thus indicating that not a great deal can be told simply by the "smell" of hops.

As to "sulphuring," there is as great a variety of opinion as in regard to the other factors which have been mentioned. It is generally believed that "sulphuring" improves the color and aids in the keeping qualities of the hop. Up to the present, however, no accurate chemical methods have been worked out for determining the amount of "sulphuring." Work on this point is now being carried out in this laboratory, and although only preliminary results are available at this time, we are certain that little can be told regarding the actual amount of "sulphuring" by simply observing the physical appearance of the hop.

Certain subconscious factors often influence the estimation of aroma and the other constituents of hops. Chief of these, perhaps, is geographical origin. The belief that hops grown in certain localities are superior, has become so prevalent as to have a subtle influence on the buyer or the consumer. This fact may be illustrated by citing an incident which occurred several years ago. Some men who had just planted hop yards in the State of Idaho were very enthusiastic over the quality of their product, and after the hops were

baled, they labeled them in large letters: "Choice Idaho Hops." The hops were then shipped to New York City to be sold. One dealer after another tried to dispose of the shipment, but in vain. The consumers and the buyers had never heard of Idaho hops and that fact was enough to keep the shipment from selling. Finally, a dealer removed the baling cloth and replaced it with cloth bearing the label: "Choice Oregon Hops." He sold the entire shipment at once for the highest market price.

Dr. W. W. Stockberger, of the United States Department of Agriculture, who has given some attention to standards for the valuation of hops (Circular No. 33, Bureau of Plant Industry), states:

"The chaotic condition of existing ideas with respect to hop aroma and quality, together with the necessity for their thorough revision, is illustrated by the following opinions, each from a different specialist in the use of judgment of hops:

"Saaz hops are best.

"The idea of the superiority of the foreign hop is largely a matter of prejudice.

"German hops are unquestionably best.

"Kent hops are the finest; they are better than the German.

"The Wisconsin hops are as good as the German.

"German hops are best because of their fine aroma. A pound of German hops is worth three pounds of American.

"The best New York hops are practically as good as the German.

"The shrewd dealer can sell anything that looks like a hop.

"Since hops of different geographical origin have different flavors, naturally individual preferences become established.

"The present method of judging hops is a very doubtful one; prejudice or taste plays the larger part.

"Pacific Coast hops are stronger in preservative resin than English hops.

"American hops can never equal the German, but they can be greatly improved.

"So far as general quality is concerned, if New York hops were as carefully picked and handled as the foreign hops they would equal the German in quality.

"Differences between American, English, and German hops are almost entirely a question of flavor.

"German hops have much more lupulin than the American.

"There is a wide difference in the quality of German hops. New York hops grown from German roots are better than the poorer grade of German hops.

"Quality really does not amount to much. Salesmanship rather than quality counts. Hops are frequently bought as one kind and sold as another.

"Pacific Coast hops contain more lupulin than foreign hops.

"English hops are superior to the German hops. The superior flavor ascribed to the German hop is chiefly a question of preference.

"German hops have a superior flavor, but are not so superior to the American hops as has been generally supposed.

"The best Pacific Coast hops are as good as the German or Bohemian hops.

"The uncertainty of the results of physical examination, and the difficulty of determining quality in hops by inspection, has been long recognized in Germany, where many safeguards have been adopted to secure authenticity in the representation of the origin of their hops. That the hop trade recognizes and plays upon these prejudices is shown by the following statement of Emanuel Gross (Gross, E. Hops, pp. 315, 320. 1900):

"It is justly alleged against certain dealers that they falsify the origin of their hops. * * * A prominent part is now played by the numerous associations for securing a proper guarantee of the origin of hop parcels. Certain unscrupulous dealers have made fortunes by falsifications of this nature; viz., buying small quantities of, say, fine Saaz hops, mixing them with larger amounts of hops from other districts * * * and selling the whole as Saaz hops.

"The regulations existing in Germany and Austria under which packages of hops are sealed and accompanied by a certificate in order that their origin may be guaranteed in the interests of both growers and consumers, and the requirement in England that hops must be branded with the name and address of the grower, appear to indicate a widespread inability on the part of consumers to judge the quality of hops."

From the standpoint of the work of this station and the limited facilities afforded, we have not deemed it advisable to go into any extensive work on the development of hop standards. The writers believe that this is a matter which should

be worked out in co-operation with other experts from this and perhaps other countries. It is a large problem, and its ultimate solution will no doubt be the result of the work of several investigators. This work has already been begun, indeed, in a preliminary way, by the scientific committee of the International Barley and Hop Prize Exhibit of Chicago.

Considering everything, it seems that the principal use of the hop commercially is for its flavoring and preservative qualities. Investigations have shown that these qualities are dependent upon the soft bitter resins. For this reason, accurate determination of these constituents is surely a matter which should receive first consideration in the valuation of hops. Again, the soft bitter resins change during storage to the hard, worthless resin (gamma resin), and hence the determination of the latter should also be considered. It may be that the amount of tannin and also the amount of "sulphuring" are of more or less significance. At any rate, it seems that in any scheme for the correct valuation of hops the quantitative analytical determination of certain constituents cannot be omitted. This fact is becoming recognized more and more, and chemical analyses of hops are now being made by a number of consumers. Doctor Alfred Fischer, who is a member of the scientific committee of the International Barley and Hop Prize Exhibit and a man thoroughly in touch with the industry in which hops find their widest use, has recently made the statement:

"I believe that a basis should be found for the creation of standards for the chemical analysis of hops. There is no doubt that the present methods already enable us properly to judge hops for their commercial use."

With the same idea in mind, the writers began, in the autumn of 1910, some preliminary work comparing the ordinary commercial grading with the results obtained from the quantitative determination of foreign matter, hard resin, and soft bitter resins. Samples were secured from an experienced hop buyer and grower who had been buying hops on the Oregon market for many years. The samples were graded by this judge and immediately sent to the chemical laboratory, where the analytical determinations were soon made. Other

samples were again secured in the autumn of 1911 from this same judge and tested out as before. At this time samples were also obtained from two other experienced judges and subjected to analysis. All of the specimens were of Oregon-grown hops and of English Cluster variety. The results of the investigations are tabulated in Table VII. The judges are not named, but they are designated as judges No. 1, No. 2 and No. 3.

TABLE VII.

COMPARISON OF COMMERCIAL AND SCIENTIFIC METHODS OF JUDGING.

Judge	Sam- ple No.	Year	Commercial Rating	For- eign Matter	Total Resins	Soft Bit- ter Resins	Hard (gam- ma) resin
				%	%	%	%
1	1	1910	Strictly prime	3.73	16.00	14.15	1.85
1	2	1910	Prime	2.72	15.95	13.77	2.18
1	3	1910	Good medium	11.14	16.66	14.50	2.16
1	4	1910	Prime	4.94	17.37	15.52	1.85
1	5	1910	Medium	4.03	17.21	15.28	1.93
1	6	1910	Medium	6.96	13.46	11.62	1.84
2	7	1911	Prime	2.80	19.04	17.23	1.81
2	8	1911	Choice	3.80	19.46	17.48	1.98
2	9	1911	Poor	5.00	17.32	15.62	1.70
3	10	1911	Prime	1.40	19.42	16.92	2.50
3	11	1911	Good prime	6.40	19.29	17.10	2.19
3	12	1911	Choice	1.20	19.98	16.78	3.20
3	13	1911	Prime	3.20	20.19	15.96	4.23
3	14	1911	Prime	2.40	20.49	17.62	2.77
1	15	1911	Fancy	2.40	16.96	14.97	1.99
1	16	1911	Prime	4.40	18.83	16.77	2.91
1	17	1911	Prime	2.80	17.23	15.92	1.31
1	18	1911	Choice	2.80	19.42	16.62	2.80
1	19	1911	Prime	6.00	19.30	17.20	2.10

NOTE: The terms used in the commercial grading rank in the following order: Fancy, strictly choice, choice, strictly prime, prime, good medium, medium, poor.

From what has been said before, any extensive discussion of the results here reported is unnecessary. Suffice it

to say, that some samples which are graded "medium" contain less foreign matter than others graded "prime" or "strictly prime"; sample 15, which is graded "fancy" by judge No. 1, contains less soft bitter resins than sample graded "poor" by judge No. 2; the greatest amounts of hard resin are to be found in samples 12 and 13, which are graded "choice" and "prime," respectively. A thorough study of the results indicates that mere physical inspection of a sample is not reliable even in determining the quantity of foreign matter, and much less so in determining that of soft bitter resins and of hard resin.

In conclusion, the writers desire to say that the adoption of scientific standards for hop valuation are of much importance to the hop grower. Before any marked improvement can be made in the quality of hops there must be some definite standard to work toward. Furthermore, when it is considered that the American hops are judged as to quality in our own markets by a standard based largely upon the characteristics of hops imported from Europe, it seems that the hop growers should avail themselves of every opportunity to further the working-out and adoption of scientific standards of valuation which are based entirely upon intrinsic value and without reference to other factors. When such standards are in use, we venture to predict that our Pacific Coast hops will be more favorably looked upon in our markets than they are at the present time.

SUMMARY.

1. Field tests of the effect of certain different commercial fertilizers on the growth of hops in some of the older yards have been tried. General observations have also been made of the efficiency of commercial fertilizers and barn-yard manure on a number of yards. The results obtained, while not extensive or complete, indicate that the commercial fertilizers tried cannot be used profitably in the culture of hops in the Willamette Valley. Barn-yard manure is the best fertilizer yet found for the purpose.
2. A comparative study has been made of available methods for the quantitative determination of the total soft bitter resins and the hard resin in hops. All the methods tried have been found faulty with the exception of the modified Lintner volumetric method for the determination of total soft resins. New methods have been devised which overcome the defects of existing methods.
3. A study has been made of the effect of kiln-drying at 145° Fahr. on the composition of the hop. It has been found that, contrary to the belief of many, there is little if any change in the composition of hops when dried at this temperature.
4. The composition of the hop at different stages of ripeness has been determined. The results show that there is a continuous increase in the amount of soft bitter resins throughout the ripening period. The ratio of the alpha to the beta resin changes very much during the ripening period, the alpha resin increasing more rapidly than the beta. There are no marked changes in the amounts of hard resin, wax, and tannin as the hop increases in ripeness. From the data obtained, there is no evidence that one constituent changes over to the form of another during the process of ripening.
5. A comparative study has been made of the composition of hops from different countries. The opinion that hops from certain localities are superior to our Pacific Coast hops

is not borne out by the results. The work which has been done indicates that Oregon-grown hops have as great if not greater content of soft bitter resins than hops grown in any other part of the world.

6. The deficiencies of present standards of judging have been presented and the need of definite scientific standards has been pointed out. Results have been offered to show that mere physical inspection is not reliable in determining the quantity of foreign matter and much less the quantity of soft bitter resins and hard resin.