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Some Chemical Changes Involved in the Formation of
Various Kinds of Silage.

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The object with which the work upon the chemical changes involved in the formation of various kinds of silage was started was to follow out in a more complete manner than had heretofore been done some of these quantitative chemical changes. On account of the large amount of time necessary for the working out of anything like a complete set of analyses, the number of analyses made is not as great as is to be desired before anything in the nature of a sound basis for definite conclusions is reached. These analyses are for this reason offered more as a step in the general progress of knowledge concerning those silage materials under consideration, than as any attempt to settle beyond question the composition of any one form of silage.

The question of the composition of silage of different kinds, and the changes undergone by the plant in the process of silage formation, has been attacked by various investigators from several angles since the very beginning of the science of agricultural chemistry. The more generally used silage plants have been quite thoroly investigated. Since the changes undergone by alfalfa and alfalfa mixtures in forming silage seemed not to have been much stud-

ied these were selected for the work.

Most of the analyses of alfalfa silage found in the literature are in the nature of the regular cattle feeds analyses (1) made before and after the material had been ensiled. One of the analyses of this character is given by Tangl and Weisen (2).

	Water	Crude Protein	Fat	Fiber
Fresh	13	14.35	3.38	20.65
Silage	48	10.62	1.63	10.31

They found that on the dry basis there was an increase in amido bodies, pure protein remained the same, and there was a loss in other nutrients. True, Woll and Dolcini (3) give the following figures for alfalfa silage:- Moisture 76%; protein 3.4%; fat .34%; fiber 5.56%; ash 2.98%; volatile acids .4%; fixed acid .91%.

Reed and Fitch (4) give the following analysis for alfalfa and alfalfa silage:-

	Moisture	ash	Prot	Fiber	Fat
Fresh Alfalfa	42.79	6.99	11.00	13.55	1.69
Alfalfa Silage	45.61	6.29	10.63	13.34	2.81
Fresh Alfalfa	62.75	4.60	6.94	10.32	1.76
Alfalfa Silage	67.23	4.17	5.51	9.75	11.11

E J Russell (5) worked out in detail the various products found in the finished silage made from

corn. His work was mainly of a qualitative nature.

Dox and Neidig (6) have developed a quite extensive study of the changes in silage from a quantitative point of view, but their work is chiefly upon corn silage.

Methods of Analyses:- The general series of analyses were made upon each sample in most cases. The first of these was the regular cattle foods (2) analysis outlined on pages 57-58 of Bulletin 107, issued by the Bureau of Chemistry, U. S. Dept of Agri. This consisted of analysis for total moisture, ash, crude fat or ether extract, crude fiber, crude protein, pure protein and amide-nitrogen. The second series consisted of analysis by special methods designed for investigation of silage problems.. These methods were gradually added to as the work progressed, so that in some of the earlier analyses data from some of the methods is lacking.

The method of sampling the small experimental silos was, first to discard the spoiled silage at the top, then to completely empty the silo, samples of about a peck being collected at every foot in the good silage.. In the case of the cans the whole can was emptied after being freed from spoiled silage, and the contents used in the same way as the composite samples from the small silos. The large sample secured by one

of the above methods was next mixed thoroughly and quartered down until the desired sample was left. This was divided into three parts. One was allowed to dry in the air and later ground and the sample taken from it for the cattle foods analysis. The second part was placed in a fruit press and the juice extracted from it and used for analysis. The third part was finely ground through a food chopper and this was then used for still other analyses. The following outline will give a clear idea of the methods used:-

Sample of Silage divided into three parts.

I - One part was dried in the air and analyzed by methods for cattle foods analysis. (Bul. 107/). (2).
 a. Moisture;; b. Ash;; c. Crude protein;; d. Pure protein;
 e. Amido-nitrogen; f. Crude fat; g. Crude Fiber.

II - Juice was expressed from one part and analysis made for

- | | |
|------------------------|------------------------|
| a. Total acidity | b. Volatile acidity |
| c. Formic acid | d. Lactic Acid. |
| e. Total nitrogen | f. Ammonia nitrogen |
| g. Amino acid nitrogen | h. Albumenoid nitrogen |
| i. Amido-nitrogen | j. Specific gravity |
| k. Sugars. | |

III - A third part was again subdivided.

A. Unground original silage.

1. Total moisture. 2. Air dry moisture.

B. Ground original silage.

1. Total nitrogen. 2. Sugars.

Each determination will be briefly described in the following paragraphs.

Air dry moisture - Determination of the moisture lost on exposure to the air in the drying room at ordinary temperatures for about two weeks. Made upon the original sample.

Total moisture - Moisture loss on heating in the oven at 100° until constant weight of the sample was reached. Made upon the original sample.

Total acidity - Two methods were used at first. In the one a part of the ground fresh sample was divided into two 100 g. samples. These were then made up to a volume of 500 cc ^{with CO₂-free distilled water. This volume was then placed in large bottles and} more of the CO₂-free water added making 500 cc a total volume of 1000 cc. The bottles were placed in a shaker and shaken for one hour. Part of each was then filtered off and 50 cc samples used for titration against .1N-NaOH (Indicator -Phenolphthalein). The calculation of the acidity was made on the assumption that 100 grams of silage occupy 30 cc. (7). The second method used was to take 100 cc of the expressed juice and make it up to 500 cc with CO₂-free, distilled water. 10 cc samples of this material, further diluted, were used in the ti-

titration.. The acidity in both cases was calculated in grams of acetic acid. It was found after several trials that the results of both methods checked very closely, so that the first method, which requires more time, was discarded.

Volatile acids - From the sample of juice two 100 g. charges of juice were taken. In the earlier analyses 5 cc of concentrated H_2SO_4 diluted with 45 cc of water was next added to acidify the juice and liberate any combined acids.. In the later analyses 5 g. of tartaric acid were used in-
as some trouble was experienced with the H_2SO_4
stead of the H_2SO_4 being carried over with the volatile acids and steam. The samples were then subjected to steam distillation in a partial vacuum at a temperature of $70^{\circ} - 80^{\circ} C$. The distillation was considered complete when a 500-700 cc sample of distillate required 2 cc or less of .1N-NaOH to neutralize it. No attempt was made to determine the various volatile acids present since the Duclaux method was shown to be unsatisfactory for this purpose (8).. Instead the volatile acids were neutralized with a .5N-NaOH and calculated in grams of acetic acid, thus obtaining a basis for comparison..

Formic Acid - The neutralized distillates from the volatile acid determinations were reduced to volumes of less than 100 cc. They were then acidified with the calculated amount of H_2SO_4 and redistilled three times in order to obtain a fairly pure distillate. These

distillates were again neutralized with NaOH and then evaporated to dryness. The residues were taken up with small volumes (50-100 cc) of distilled water and filtered if not clear. Concentrated Hg Cl_2 solution was added in excess and the solutions heated from one to two hours over the water bath. The formic acid reduces the Hg Cl_2 to Hg Cl which is precipitated. The Hg Cl precipitates were filtered off in Gooch crucibles, washed with distilled water, and dried at 100° to constant weight. The weight of $\text{Hg Cl} \times .0976 =$ formic acid present.

Lactic acid - The method used was essentially that of Dox and Neidig (9). The samples of juice from which the volatile acids had been removed were extracted in separating ^{dry} funnels with 100 cc portions of ether until the solution obtained by evaporating off the ether from a single extraction and taking up with water required less than 2 cc of $.1N\text{-Ba(OH)}_2$ to neutralize it (20-25 times). The ether was then removed from the combined extracts of each sample and each was diluted with about 100 c.c. of water. Then an excess of Ba (OH)_2 was added and the solution boiled. The excess was then exactly neutralized with $\text{H}_2 \text{SO}_4$ and the Ba SO_4 filtered off. The calculated amount of ZnSO_4 was added to the filtrates and the BaSO_4 again removed. The solutions were then evaporated down until crystals of zinc lactate began to form whereupon they were removed and allowed

to stand until crystallization was complete. The crystals were filtered off into Gooch crucibles and washed with a small volume of cold water and dried at 100° to constant weight. A second and third crop of crystals were generally obtained from the mother liquor. The combined weight of the crystals of zinc lactate from the three crops was taken as the yield from the sample and the amount of lactic acid calculated from it.

Total nitrogen - This was the regular Kjeldahl (1) determination made upon 10 gram samples of ground silage and 10 c.c. samples of the juice.

Ammonia nitrogen - 10 cc samples of juice were placed in Kjeldahl flasks and diluted with 300-400 c. c. of distilled water. 5 grams of magnesium oxide were then added to each sample. A small piece of paraffin was placed in each flask to prevent frothing and the solution was then distilled for two hours, the N H_3 being caught in H Cl . The excess of H Cl was determined by titration with standard NH_4OH solution and the ammonia of the sample calculated as in the regular nitrogen determination.

Amino acid nitrogen - The method used was an adaptation of Sorenson's (10) formaldehyde reduction method. The total acidity of the juice was first determined as previously described. Then 10 c.c. samples of the solution made by diluting 100 c.c. of juice to 500 c.c. with CO_2