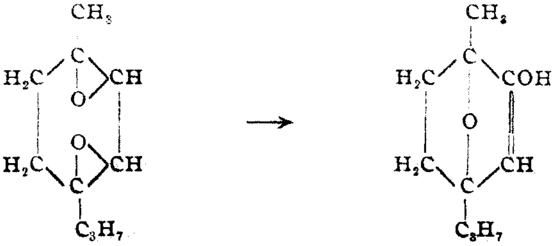
bonyl group seems therefore improbable. Considering the question of stability together with the fact that, as will be shown, carvacrol is obtained as a product of the dehydration of the glycol anhydride, it seems altogether probable that it results from the rearrangement of the anhydride in the following manner:



Glycol anhydride. "Oxy" phenol.

Dehydration of the Glycol Anhydride.—In an attempt to form an ester by the direct union of the glycol anhydride with benzoic anhydride, the mixture was heated to 150°. The expected result was not obtained, water being split off and a phenol ester obtained, from which the phenol was isolated and purified by solution in 5% potassium hydroxide. This phenol proved to be carvacrol. Analysis agreed with the formula $C_{10}H_{14}O$. Sp. gr. 20° 0.9756 n_D 20°, 1.522. Phenylurethane, m. 140°. The yield amounted to about 25%.

THE VOLATIL ALIPHATIC ACIDS OF CORN SILAGE.

By Arthur W. Dox and Ray E. Neidig.

Received November 18, 1912.

In view of the recent publication in This Journal of an article by Hart and Willaman[1] entitled "Volatil Fatty Acids and Alcohols in Corn Silage," it is thought advisable to call attention to a previous publication of our own[2] on the same subject. The present paper is not simply a claim to priority on the part of the authors, but an endeavor to explain the discrepancy between our results and those obtained by Hart and Willaman.

The method used by Hart and Willaman in preparing their sample for the Duclaux determination is briefly as follows: The silage was first ground in a food chopper. One hundred grams were suspended in two liters of water, 10 cc. of concentrated sulfuric acid were added and the solution was distilled in a current of steam until a distillate of three liters was collected. The distillate was neutralized with barium hydroxide

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[1] This Journal, 34, 1619–25 (1912).

[2] Dox and Neidig, "The Volatile Aliphatic Acids of Corn Silage," Iowa Agricultural Experiment Station, *Research Bulletin* 7, 32, June, 1912. This publication may be had free of charge upon application to the authors or to the Director of the Iowa Agricultural Experiment Station, Ames, Iowa.

and the free alcohols recovered by distillation. The barium salts were further concentrated, and the free acids divided into several fractions by distilling off 100 cc. after each addition of 20 cc. decinormal sulfuric acid. Each fraction was then examined by the Duclaux method. The alcohols were likewise determined after oxidation to the corresponding acids.

From the results obtained by this method of procedure, Hart and Willaman concluded that "of the total volatil acids 17% was formic, 75% was acetic, 8% was propionic, and 0.6% butyric," also that "of the total alcohols 21% was methyl, 72% was ethyl, and 7% propyl." In a footnote they state, however, that "while the methods of analysis used showed the presence of methyl alcohol, it is barely possible that the formic acid may have arisen from the oxidation of substances other than this alcohol."

This corroborates our work in so far as the relative amounts of acetic, propionic and butyric acids are concerned and also with regard to the relative amount of ethyl and propyl alcohol. We found however, *only traces of formic acid and no evidence whatever of methyl alcohol.*

In our preliminary studies we proceeded as did Hart and Willaman, but we soon abandoned this method on account of three obvious sources of error, which will be discussed briefly in the following paragraphs.

(1) When the steam distillation is carried out at atmospheric pressure, the lactic acid which is normally present in silage, passes over in appreciable amount into the distillate, and it is practically impossible to reach a point where the distillate is neutral. The following protocol will serve by way of illustration:

Lactic acid equivalent to 178.75 cc. decinormal barium hydroxide was distilled from a liter flask in a current of steam at ordinary pressure. Eight liters of distillate were collected and titrated separately.

Distillate.	Cc. 0.1 N $Ba(OH)_2$.
1st liter	4.6
2nd liter	3.6
3rd liter	3.6
4th liter	3.2
5th liter	3.2
6th liter	2.8
7th liter	2.8
8th liter	2.4

The lactic acid that passes over then appears in the Duclaux calculation as formic acid. When 110 cc. of lactic acid equivalent to 39.4 cc. of decinormal barium hydroxide were subjected to the Duclaux fractionation, 5.8% of this acid passed over in the 100 cc. distillate. From the titration figures we calculated the Duclaux constants for lactic acid, which are given below in line A. Lines B and C are Duclaux's constants for formic and acetic acids, respectively.

	10 cc.	20 cc.	30 cc.	40 cc.	50 cc.	60 cc.	70 cc.	80 cc.	90 cc.	100 cc.
A.......	6.5	13.0	19.6	26.1	32.6	41.3	50.0	58.7	69.6	100
B.......	5.9	12.2	19.0	26.4	34.4	43.2	52.8	64.6	79.6	100
C.......	7.4	15.2	23.4	32.0	40.9	50.5	60.6	71.9	84.4	100

From the above it is evident that the constants for lactic acid are lower than those for formic acid, and a given amount of lactic acid would appear in the calculation as a *greater* amount of formic.

(2) Inasmuch as the volatil acids are present in silage for the most part in the free state, the addition of 10 cc. concentrated sulfuric acid to two liters of the suspension (practically 1% sulfuric acid) is not only unnecessary, but highly objectionable. It is a well known fact that the hexose sugars, which are present in silage or could easily result from hydrolysis of the starch, are decomposed by mineral acids into levulinic acid and formic acid. The formic acid thus produced would distil over and perhaps also some of the levulinic.

(3) When suspended particles of silage are distilled, the recovery of volatil acid is necessarily slow on account of the time taken for diffusion into the surrounding medium. This would account, in part at least, for the difficulty mentioned by Hart and Willaman in obtaining a neutral distillate after collecting three liters. Another objection to using a suspension of silage is that the cellulose, pentosans and other insoluble matter are subjected to the action of the sulfuric acid. Hart and Willaman find aldehyde in their alcoholic fraction. In our own experiments under the same conditions we found considerable furfural. This, on oxidation, would yield pyromucic acid, which would pass into the distillate and probably be calculated into methyl alcohol.

In our work these sources of error were practically eliminated, (1) by making the steam distillation under diminished pressure at a temperature of 80–85°; (2) by reducing the amount of sulfuric acid; and (3) by distilling silage juice obtained by the use of a Büchner press instead of one containing suspended particles of silage.

The superiority of this method is illustrated by the following data:

	New method. 0.1 N $Ba(OH)_2$. Cc.	Old method. 0.1 N $Ba(OH)_2$. Cc.
1st liter................	102.0	66.6
2nd liter................		36.1
3rd liter................	6.0	19.3
4th liter................	1.5	14.0
5th liter................	...	11.3
6th liter................	...	9.0
7th liter................	...	8.1
8th liter................	...	6.9

Although the above comparison was made with different samples of silage, the greater ease in obtaining a rapid and complete recovery of the volatil acid by the modified method is apparent.

This method was applied to the examination of fifteen samples obtained at intervals from three distinct types of silos. We found acetic and propionic acids in the ratio of about ten to one, butyric acid in considerable amount only in samples where some slight indications of spoiling were otherwise apparent and formic acid usually only in traces. By fractionally distilling some 300 cc. of pure acids extracted from silage and identifying the acids by their boiling point, the same results were obtained. We found also ethyl and propyl alcohols in the proportion of about ten to one, but no evidence whatever of methyl alcohol. Our average for the total volatil acid was 1% formic, 87% acetic, 8.7% propionic, 3% butyric, and 0.3% valeric, and for the total alcohols, 90% ethyl and 10% propyl. Although, as Hart and Willaman maintain, no two silages are exactly alike in composition, the differences between our results and theirs, with regard to the presence of relatively large amounts of formic acid and methyl alcohol, can hardly be explained on this assumption.

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NOTES.

Ethyl Ether by Catalysis.[1]—Sabatier and Mialhe[2] have shown that several metallic oxides (thoria, alumina, and tungsten) exercise a "catalytic action" on alcohols between 300° and 350°. It would appear from their investigations that this action is almost entirely that of dehydration with the separation of ethylene, although, when operating at a lower temperature, the dehydration is said to be incomplete and to be capable of limitation to the production of ethyl oxide.

The dehydration of ethyl alcohol in the presence of thoria has been studied in this laboratory[3] and the results obtained show some variance with those of Sabatier and Mialhe. The contributions of these authors are not very explicit as to experimental details, but we endeavored to observe all the conditions necessary for the production of ethyl ether by partial dehydration, according to the reactions:

$$2C_nH_{2n+1}OH + ThO_2 = H_2O + ThO(OC_2H_{2n+1})_2;$$

$$ThO(OC_nH_{2n+1})_2 = ThO_2 + (C_2H_{2n+1})_2O.$$

The apparatus used in our experiments, illustrated herewith, consisted essentially of a jacketed porcelain tube containing glass beads covered with pure thoria, heated in a combustion furnace, and over which

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[1] Read at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] *Compt. rend.*, 150, 823; see also *Idem.*, 149, 995; 150, 1217; 161, 359, 492.

[3] The experimental work was carried out by Messrs. Barnett Cohen and Alfred V. Salamon.