

complete, make immediate duplication impossible. The results, however, are close enough to show that there probably exist certain chemical similarities in organisms which morphologically are widely different. It seems not impossible that study of bacterial action from the side of chemistry may lead to a different conception and a truer understanding of the nature of the virulence and the toxicity of microorganisms.

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### VOLATILITY OF LACTIC ACID.

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Received May 19, 1913.

In a recent article by Dox and Neidig<sup>1</sup> our methods for the determination of the volatil acidity of silage were criticized on three different grounds. First, because when distilling in steam at ordinary pressure a quantitative removal of the volatil acids is not possible, because even after eight liters of distillate are collected the distillate is not neutral. Second, because lactic acid keeps coming over in appreciable quantities, and is titrated as volatil acid. Third, because this lactic acid, when distilled according to Duclaux' method for estimating the volatil fatty acids, produces a curve very comparable to formic acid, and the figures for formic acid are thus always raised to the extent of the lactic acid that comes over. They reported experimental data to support their criticisms, of which the following are the most important:

"Lactic acid, equivalent to 178.75 cc. 0.1 *N* alkali, 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 <i>N</i> Ba(OH) <sub>2</sub> .
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 calculations as formic acid. When 110 cc. of lactic acid equivalent to 39.4 cc. of 0.1 *N* barium hydroxide were subjected to the Duclaux fractionation, 5.8% of this acid passed over in the 100 cc. of distillate. From the titration figures we calculated the Duclaux constants for lactic acid,

<sup>1</sup> THIS JOURNAL, 35, 90 (1913).

	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	100.0
B.....	5.9	12.2	19.0	26.4	34.4	43.2	52.8	64.6	79.6	100.0

which are given above in line A. Line B is Duclaux' constants for formic acid."

Their first criticism, that a neutral distillate from silage cannot be obtained at atmospheric pressure, is unquestioned, and a fact well known to us. But the reason for it is not so much the volatility of lactic acid as it is the failure of formic and acetic acids to volatilize quantitatively from dilute solutions.

The statement that lactic acid is appreciably volatil has also appeared in papers by Jensen,<sup>1</sup> Neuberger and Rosenberg,<sup>2</sup> Welde<sup>3</sup> and others.

To determine whether lactic acid is appreciably volatil, and whether it can be distilled in sufficient quantities for the calculation of a Duclaux curve, the following experiments were conducted.

An apparatus for distilling in steam was set up, using a sheet-iron can of four liters capacity for the production of the steam, a two-liter flask for the distilling solution, and a four-foot condenser. Ordinary distilled water was put in and distilled for 2 hours to free it from carbon dioxide. At the end of that time 500 cc. of distillate were titrated as a blank, and required 1.75 cc. 0.1 *N* alkali to produce an end point with phenolphthalein, showing that carbon dioxide had not been entirely removed. Then lactic acid, equivalent to 41.4 cc. 0.1 *N* alkali, was introduced into the distilling flask, containing about 1000 cc. of water, and the distillation continued with the following results:

#### Distillation (1)

1st liter.....	2.50 cc. 0.1 <i>N</i> alkali
2nd liter.....	1.75 cc. 0.1 <i>N</i> alkali
3rd liter.....	1.25 cc. 0.1 <i>N</i> alkali
4th liter.....	4.70 cc. 0.1 <i>N</i> alkali
5th liter.....	2.25 cc. 0.1 <i>N</i> alkali

Between the third and fourth liters the steam boiler had to be refilled, and the rise in titer of the distillate shows an increased amount of carbon dioxide. These figures convinced us that no conclusive data concerning the volatility of lactic acid could be secured without using every precaution to free the steam from all titratable contaminations.

Water free from carbon dioxide was prepared by aspirating through it air which had been exhausted of carbon dioxide by passing through a long tube of soda lime. After 24 hours the water was so free from carbon dioxide that three drops of 0.1 *N* alkali in one liter gave a distinct pink color that was permanent for thirty seconds, which was always used.

<sup>1</sup> *Landw. Jahrb. Schw.*, 18, 314 (1904).

<sup>2</sup> *Biochem. Zeit.*, 7, 178 (1907).

<sup>3</sup> *Ibid.*, 28, 504 (1910).

as the standard. This water was used in both the boiler and the distilling flask. The four-liter boiler was replaced by one holding twelve liters, and a distilling head was inserted between the distillation flask and the condenser to prevent any acid being carried over mechanically. This form of apparatus was used in all the following distillations. A liter of blank was always distilled before the introduction of any acid so as to insure a neutral medium. The best blank that could be prepared required 0.15 to 0.20 cc. 0.1 *N* alkali to produce an end point. In the table this blank is subtracted from the titer as found. Lactic acid from two different firms—Kahlbaum and Merck—was used, so as to detect by comparison the presence of any volatil impurity. Different amounts of the acid were also used, to study the effect of concentration on the volatility. The data secured are given in Table I.

TABLE I.—VOLATILITY OF LACTIC ACID.

Source of acid.	No. of distillation.	Total acid present.	Titre of each liter.	Per cent. of total acid distilled in 4 liters.
Kahlbaum.....	2	41.4 cc. 0.1 <i>N</i>	1st 0.50 cc. 0.1 <i>N</i> 2nd 0.75 3rd 0.30 4th 0.45	3.38
Merck.....	3	44.4 cc. 0.1 <i>N</i>	1st 0.25 2nd 0.80 3rd 0.45 4th 0.35	2.82
Merck.....	4	173.4 cc. 0.1 <i>N</i>	1st 0.50 2nd 2.00 3rd 0.50 4th 0.80 5th 0.50 6th 0.75	1.06
Merck.....	5	948.8 cc. 0.1 <i>N</i>	1st 2.20 2nd 2.10 3rd 2.35 4th 2.80	0.93
Prepared pure acid.....	6	64.0 cc. 0.1 <i>N</i>	1st 0.25 2nd 0.35 3rd 0.25 4th 0.25	0.78
Prepared pure acid.....	7	192.0 cc. 0.1 <i>N</i>	1st 0.45 2nd 0.45 3rd 0.37 4th 0.35	0.53

The lowest amount used represents approximately what would be found in the distillation of a sample of silage; the next amount is more nearly that used by Dox and Neidig in their experiment, as they do not state definitely the dilution in the flask.

To test further the impurity of the purchased acids some pure lactic acid was prepared. This was done by boiling the commercial C. P. acid with zinc oxide, recrystallizing the zinc salt several times, and then freeing the acid by means of washed hydrogen sulfide. The purified zinc lactate on ignition gave 33.39% ZnO; theory 33.33%. The volatility of this acid was then determined, as shown in Table I.

It is evident from these data that lactic acid is but slightly volatil at ordinary pressure, and not nearly so volatil as the experiments of Dox and Neidig would indicate. In fact, in considering the sensitiveness of phenolphthalein to carbon dioxide and the difficulty of preventing contamination by it, it seems probable that most of the titer in the steam distillate that has been credited to lactic acid is due to carbon dioxide. The following considerations point to this conclusion.

In comparing distillations 1 and 2, the difference in titer is most certainly due to the difference in the carbon dioxide content of the water used.

In considering Dox and Neidig's figures, it should be noticed that the titer of each liter decreases on the average by 0.58%, while the concentration of the distilling acid solution decreases with each liter by only 0.15%. The question then may well be asked, why, if it was lactic acid alone coming over, did not the same amount of acid distil in each liter, since the concentration remained practically the same? Further, if carbon dioxide were present, it would come over in decreasing quantities as the distillation continued, and that is just what Dox and Neidig found.

The radical difference in the volatility of lactic acid as found by Dox and Neidig, and by ourselves when perfectly carbon dioxide-free water was used, can be explained in no other way than by the presence of carbon dioxide in their distillation liquids.

To determine the validity of Dox and Neidig's third criticism, that lactic acid has a Duclaux curve very similar to that of formic acid, a number of distillations were made and the curves computed. First, carbon dioxide-free water was distilled and titrated with barium hydroxide (0.1 *N* factor 0.606) to insure accuracy of results. When the distillate showed no titer, this water was used in making up the lactic acid solutions for the subsequent distillations. In distillation A, the prepared pure lactic acid equivalent to 14.08 cc. 0.1 *N* alkali was diluted to 110 cc., distilled, and each 10 cc. portion titrated with barium hydroxide. In B and C, Kahlbaum's lactic acid was used. D represents formic acid.

	Total acid present.	Per cent. of total in 100 cc. distillate.
A.....	14.08 cc. 0.1 <i>N</i>	2.3
B.....	38.41 cc. 0.1 <i>N</i>	2.8
C.....	112.00 cc. 0.1 <i>N</i>	3.0
D.....	.....	59.0

In A the titer for the whole 100 cc. was only 0.54 cc. of barium hydroxide, which was too small for the calculation of a curve. In B the titer was 2.35 cc. and in C, 5.61 cc., for which the following curves were calculated:

	10 cc.	20 cc.	30 cc.	40 cc.	50 cc.	60 cc.	70 cc.	80 cc.	90 cc.	100 cc.
B.....	1.7	4.2	6.8	11.0	16.1	23.8	32.3	45.1	65.1	100
C.....	2.3	4.9	8.3	13.0	18.5	25.8	35.4	48.4	58.6	100
D.....	5.9	12.2	19.0	26.4	34.4	43.2	52.8	64.6	79.6	100

It is evident that these figures for lactic acid are not comparable to those for formic acid; nor do they agree with those reported by Dox and Neidig. The highest titer we found for the 100 cc. of distillate showed only 3.0% of the total acid, while Dox and Neidig found 5.8%; which result can again be explained only by the presence of a small amount of carbon dioxide in their solution, or by a volatil impurity in their lactic acid.

The facts presented seem to warrant the following conclusions:

1. Lactic acid is but slightly volatil in steam at 100°. The amount that passes over in the distillation of volatil acids from silage is insignificant, being equivalent to not over three or four cc. 0.1 *N* alkali in four liters of distillate.

2. Lactic acid is not sufficiently volatil to enable one to calculate a Duclaux curve for it, as only about 3% passes over in the 100 cc.

3. It is suggested that the higher results of Dox and Neidig in their experiments on the volatility of lactic acid may be due to carbon dioxide in the water used, or to volatil impurities in the lactic acid.

### NEW BOOKS.

*Traité de Chimie Minérale.* Par H. ERDMANN. Tome premier. (8vo., pp. 559.) Paris, 1913. (A. Hermann et Fils. 12 Fr.)

This is a translation by Professor A. Corvisy of the fifth edition of the well-known, excellent German work. It is a rather extensive treatise, dealing particularly with the facts and with the experimental aspects of the subject, so that it is a very useful aid to the lecturer or to the reader who wishes fuller details than are given in the ordinary text-books on the subject. Erdmann's persistence, apparently for pedagogical reasons, in retaining the atomic weights based upon hydrogen as unity, instead of those based upon oxygen as 16, will not be approved of by most chemists, but it is a matter of little importance in comparison with the generally excellent features of the work.

The first volume, now under consideration, includes an introduction of 92 pages dealing with general principles, the greater part of the space being devoted to a discussion of the metalloids (non-metals). This artificial classification has placed selenium and tellurium in separate volumes.