

This acid is formed when the 3,3-trimethylhexanoic-1,2',6 acid is heated for a short time to 200°. It appears to exist in two forms, a fumaroid and a maleinoid form. Only the former has thus far been obtained pure. The acid was purified by crystallization from water and from ether. It is difficultly soluble in cold water and in ether, almost insoluble in ligroin. It crystallizes from water or from ether in leaflets which melt at 136°.

0.1637 gram of the acid gave 0.1286 gram water and 0.3424 gram carbon dioxide.

	Calculated for C <sub>9</sub> H <sub>16</sub> O <sub>4</sub> .	Found.
Carbon .....	57.44	57.04
Hydrogen.....	8.52	8.73

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## A NEW INDICATOR FOR USE IN DETERMINING TOTAL ACIDITY OF WINES.<sup>1</sup>

BY E. G. RUNYAN.

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IN maintaining a chemical control of a beet sugar house, it is often necessary to determine by some rapid method the excess of alkali in the juices, sirups, and massecuites. The usual method is to titrate the material with a standard acid solution. As these products vary in color from a light amber to a dark brown, or nearly black, the ordinary indicators often give very unsatisfactory results, or fail entirely, on account of the difficulty of noting the end reaction.

To meet this difficulty, a French chemist, L. Lachaux, in 1892, proposed a mixture of corallin and malachite green<sup>2</sup> prepared as follows:

Three and one-tenth grams of corallin or commercial rosolic acid are dissolved in 150 cc. of 90 per cent. alcohol, neutralized and mixed with 0.5 gram malachite green dissolved in 50 cc. of alcohol. With this mixture, alkalies give a purple color, which is changed to a green by acids.

Malachite green dissolves in alcohol yielding a greenish blue

<sup>1</sup> Read before the Washington Section of the American Chemical Society, March 14, 1901.

<sup>2</sup> The zinc-double-chloride of tetramethyl-di-*p*-amidotriphenyl-carbinol, (C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> + 2ZnCl<sub>2</sub> → 2H<sub>2</sub>O.

solution, which possesses no value as an indicator by itself, but when mixed with corallin it blends with the colors of that indicator and renders the end reaction more distinct. As only the corallin in this mixture acts as an indicator, it follows that this corallin-malachite mixture can be used in titrating only those acids and bases which give a distinct end reaction with corallin alone.

Recently I had occasion to make use of this indicator in determining the amount of alkali in a highly colored sample of beet molasses and obtained very satisfactory results. It occurred to me at once that this indicator might be used advantageously in determining the total acidity of such highly colored products as wines, vinegars and ciders, since, as is well known, the present methods are far from satisfactory in the case of red or highly colored wines. The method adopted by the Association of Official Agricultural Chemists for the determination of total acidity in wines is as follows :

“ Transfer 10 cc. of the sample to a beaker, and in case of white wines add about 10 drops of a neutral litmus solution, and titrate with decinormal sodium hydroxide solution until the red color changes to violet. In case of red wines, continue adding a few drops at a time of alkali solution, until a drop of the mixture placed on delicate red litmus paper shows an alkaline reaction.”

Another method in use by some chemists is to dilute 10 cc. of the wine to about 300 cc. with boiling distilled water, heat the mixture to boiling for a moment to expel carbon dioxide, add a few drops of phenolphthalein solution and titrate with decinormal sodium hydroxide solution.

Any one who has ever tried either one of the above methods with a claret or other red wine, will, I think, agree with me that the determination of the exact point of neutrality is very uncertain.

To test the corallin-malachite indicator in comparison with phenolphthalein and litmus, three samples of wine were procured : (1) a claret, as a type of red wine ; (2) a Rhine wine for the white type ; and (3) a sherry for the medium color. In this experiment the following method was employed :

Transfer 10 cc. of the sample to a beaker, dilute with about 300 cc. of boiling distilled water, heat the mixture to boiling for a moment to expel all carbon dioxide, cool to about 75°, add 10 drops of the corallin-malachite solution, then add an excess of

decinormal sodium hydroxide solution, indicated by a purple color, titrate the excess of alkali with decinormal acid solution, adding the acid solution slowly until the appearance of a distinct green color. The change in color is best observed by transmitted light. A trial showed that it was easier to detect the transition from the alkali to the acid side than the reverse.

With phenolphthalein and litmus, slightly more of the indicator was used and the decinormal soda solution added slowly to the point of neutrality as near as that could be determined. The results are expressed as usual in terms of tartaric acid, 1 cc. decinormal sodium hydroxide solution = 0.0075 gram tartaric acid. The following are the results obtained :

## GRAMS TARTARIC ACID IN 100 CC. OF WINE.

Wine.	Corallin Malachite.	Phenolphthalein.	Litmus.
1. Claret.....	0.840	0.995	0.890
	0.870	0.980	0.920
	0.870	0.980	....
	0.880	....	....
	0.875	....	....
Average.....	0.867	0.985	0.905
2. Rhine wine.....	0.705	0.730	0.730
	0.710	0.725	0.720
	0.705	0.730	0.725
	0.695	0.735	....
	0.705	....	....
	0.705	....	....
Average.....	0.705	0.730	0.725
3. Sherry .....	0.450	0.490	0.475
	0.430	0.475	0.460
	0.440	0.475	0.460
	0.445	0.475	0.460
	0.435	....	....
	0.430	....	....
Average.....	0.438	0.479	0.464

The results obtained with corallin-malachite are invariably lower than those obtained with the other indicators, but this was to be expected when we consider that with the corallin-malachite the titration was made toward the acid reaction, and with the other indicators it was made toward the alkali side.

The greatest difference appears in the results on the claret or

red wine, where in case of phenolphthalein and litmus it was necessary to add a decided excess of alkali before the change of color could be detected. I am inclined, therefore, to believe that the results with corallin-malachite more nearly represent the true figure for total acidity of this sample.

To test the sensitiveness of the corallin-malachite, 5 drops of the mixture were added to 100 cc. of distilled water, when 0.1 cc. of 0.01 normal hydrochloric acid solution or 0.01 normal sodium hydroxide solution was sufficient to give a distinct acid or alkali reaction.

In the presence of other coloring-matters, slightly more of the standard solutions was required.

In consideration of the encouraging results obtained with this corallin-malachite mixture in my hands, I feel justified in recommending this indicator to the attention of chemists engaged in the analysis of wines, vinegars, ciders, and similar products.

## THE ESTIMATION OF CARBONIC ACID IN WATER.

BY JOSEPH W. ELLMS AND JAY C. BENEKER.

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THE estimation of carbonic acid is of considerable importance in the technical analysis of water. In the softening of water for manufacturing purposes and in the purification of public water supplies, where certain processes are employed, an accurate knowledge of the amount of this constituent is essential to a proper treatment of the water. Moreover in the sanitary analysis of sewage, of effluents from sewage purification plants, and of polluted waters generally, a determination of the amount of carbonic acid present may throw considerable light on the nature and extent of the chemical and bacterial changes which are taking place.

### CONDITION IN WHICH CARBONIC ACID EXISTS IN NATURAL WATERS.

Before discussing the methods usually employed for the estimation of carbon dioxide in water, and the principles upon which these methods are based, it may be well to consider in what forms of combination carbon dioxide exists in water and to define the different terms which are used to designate them.

The carbonates which are commonly found in natural waters are those of calcium and magnesium. The normal carbonates of