(II), 3 cc. of dimethylaniline and 2 g. of fused zinc chloride. These reagents were mixed and heated in a flask at 100° for four hours. The mixture was stirred intermittently during the heating period. The excess of dimethylaniline was then removed by distillation with steam and the waxy residue left behind washed several times with water and finally dissolved in hot alcohol. On cooling, the leuco compound separated in the form of large, colorless blocks which melted at 212–214° to an oil. The leuco compound is practically insoluble in water. The yield was 1.6 g.

Anal. Calcd. for $C_{22}H_{26}ON_4S$: N, 14.2; S, 8.1. Found: N, 14.1, 14.2; S, 7.94.

p-**2-Tetramethyldiaminodiphenyl-2-ethylmercaptothyminylmethane, VI.**—The procedure followed in preparing this new leuco compound corresponded exactly to that described in the previous experiment for the synthesis of the thio analog. The compound was insoluble in water but very soluble in warm alcohol. It crystallized from the latter solvent in long, colorless needles which melted at 218–219°. The yield was 1.8 g. from one gram of the aldehyde (III).

Anal. Calcd. for $C_{24}H_{30}ON_4S$: N, 13.2. Found: N, 13.0, 13.1.

The aldehyde used in this synthesis (III) has already been described in an earlier paper.[3]

p-**2-Tetramethyldiaminodiphenylthyminylmethane, IV.**—The aldehyde (I) used in the preparation of this compound has likewise been described in our earlier work.[3] The leuco compound was found to be insoluble in water but very soluble in boiling alcohol. It crystallized from the latter solvent in the form of flat prisms or plates and melted at 197–198°. The yield was 1.8 g. from one gram of the pyrimidine aldehyde.

Anal. Calcd. for $C_{22}H_{26}O_2N_4$: N, 14.8. Found: N, 14.9, 14.8.

Summary

1. Aldehyde derivatives of thymine condense smoothly with dimethylaniline in the presence of zinc chloride to give stable leuco pyrimidine bases corresponding to the leuco base of malachite green.
2. Their oxidation products will be investigated in this Laboratory.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION]

EFFECT OF HEAT ON MALIC ACID[1]

BY FRED W. MORSE

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During a study of the cranberry, samples of the fruit were dried before making the subsequent analysis. The berries were cut in halves, spread in thin layers on trays and placed in a large, steam-heated drying-oven, where the temperature ranged around 85°. They remained in the oven for about three days; then they were cooled in the air, weighed, ground in an iron mortar and preserved in bottles.

When total acids were determined in these samples, the results appeared to be low when compared with data obtained from fresh cranberries.

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[1] Published with the approval of the Director of the Massachusetts Agricultural Experiment Station.

More samples of cranberries were procured. Portions of each sample were weighed, cut in small pieces, placed in volumetric flasks, digested for twenty-four hours with hot water, cooled and made up to volume. Aliquots were withdrawn and titrated. Other portions of the samples were weighed, cut in halves and dried as before. The dried material was pulverized, digested in hot water and aliquots titrated.

The standard alkali used was $N/10$ sodium hydroxide and the indicator was brom thymol blue. Titrations were stopped at the greenish blue tint. The results were calculated as percentages of citric acid in the fresh berries.

Five varieties of cranberries gave an average of 2.26% of total acid in the fresh berries, while the dried portions yielded the equivalent of 1.99% on the fresh basis. Prolonging digestion of the dried material did not change the discrepancy.

The acids of the cranberry have been shown to consist approximately of four-fifths citric acid and one-fifth malic acid[2] while benzoic acid[3] is present as less than 0.1% of the fresh berries.

Nothing has been found in chemical literature to show that citric and malic acids are affected in any manner by heating below 100°. Benzoic acid does not account for the loss.

Aberson[4] and Walden[5] have shown that levo-malic acid is partially changed to the anhydride at 100 and 110°.

To ascertain the effect of temperatures below 100° upon the principal acids of the cranberry, dilute solutions of citric and malic acids were prepared from selected crystals of each. Several aliquots of each acid were titrated directly. Other aliquots were measured into small beakers. The solutions were evaporated to dryness on the water-bath. Beakers with their films of solidified acids were then placed in ovens where the temperatures were maintained approximately at the following stages: 65°, 75°, 85° and 95°. After various periods of exposure to the respective temperatures, the beakers were removed from the ovens, their contents dissolved in water and the aliquots titrated. The same standard alkali and indicator were used that were described for the cranberries. All titrations were stopped at a light blue tint.

The variations in titrating the citric acid aliquots were within the limits of experimental error, and heating the dried crystals apparently had no effect on the constitution of citric acid.

The aliquots of malic acid yielded such differing results that the crystals appeared to be affected in proportion to both temperature and time of exposure.

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[2] W. D. Bigelow and P. B. Dunbar, *J. Ind. Eng. Chem.*, **9**, 762–767 (1917); also E. K. Nelson, THIS JOURNAL, **49**, 1300–1302 (1927).

[3] G. F. Mason, *ibid.*, **27**, 613–614 (1905); also N. R. Blatherwick and M. L. Long, *J. Biol. Chem.*, **57**, 815–818 (1923).

[4] J. B. Aberson, *Ber.*, **31**, 1432–1449 (1898).

[5] P. Walden, *ibid.*, **32**, 1706–1721 (1899).

An aliquot of the original solution required 19.1 cc. of the standard alkali. Exposure of the dry acid to 65° for seventy-two hours made no change in the amount of alkali required for an aliquot. At 75° after forty-eight hours an aliquot was neutralized by 18.6 cc. of standard alkali, while another after ninety-six hours required 18.5 cc. At 85° after forty-eight hours an aliquot required 18.5 cc. and after ninety-six hours another was neutralized by 18.0 cc. At 95° 17.8 cc. neutralized an aliquot after twenty-four hours; 12.9 cc. was required after seventy-two hours and at the end of a week an aliquot was neutralized by 10.7 cc.

Walden obtained two anhydrides of *l*-malic acid. The anhydride obtained at 100° consisted of two molecules of the acid from which one molecule of water had been removed, forming a tribasic acid. The second anhydride was obtained at 180° and consisted of a double molecule with dibasic properties.

The malic acid employed in our experiments was found to be inactive to polarized light and should be regarded as *dl*-malic acid. A week's heating around 95° of a thin film of the dry acid caused an approach to the second anhydride of Walden, since the alkali required to neutralize the aliquot was but little more than half the amount required for the original solution. Under the conditions of the experiments no definite stages of dehydration were observed.

Walden found that the malic anhydride was restored to the normal acid by heating it with water in a sealed tube at 115°.

Some of the partly dehydrated aliquots were left in the beakers after titration and it was observed that the indicator tint changed to acid. Thereupon watch-glasses were placed on them and the solutions were boiled gently for a few hours with occasional additions of water to maintain the volume of solution approximately constant. The indicator tints were now strongly acid. The solutions were again titrated to the light blue tint. Enough additional standard alkali was required to bring the total for an aliquot up to 18.8 cc. in nearly every one. None could be carried above this figure.

Solutions from the five samples of dried cranberries were next heated after a preliminary titration and titrated a second time. The total alkali required by the two titrations was equivalent to 2.3% of total acid in the fresh berries, thus bringing the dried samples to equality with the undried berries.

Several other samples of dried cranberries were examined in a similar manner but not all of them could be made to yield a total acid equal to the result obtained from the corresponding undried fruit.

Summary

Summing up, malic acid is partly transformed to an anhydride when dried at temperatures between 75 and 95°, the amount of change being

dependent on both temperature and time of exposure. Solutions of the partially dehydrated acid, when neutralized by alkali and then boiled for several hours are partially and sometimes completely restored to normal strength. In conclusion, when malic acid occurs in fruits the determination of total acid will be nearest the truth when it is made on undried samples.

AMHERST, MASSACHUSETTS

[CONTRIBUTION FROM THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

CONDENSATION OF GLUCOSE AND FRUCTOSE. SYNTHESIS OF AN ISO-SUCROSE[1]

BY JAMES COLQUHOUN IRVINE, JOHN WALTER HYDE OLDHAM AND ANDREW FORRESTER SKINNER

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The investigation of which the results are now communicated has been in progress for some years and was designed to effect the synthesis of sucrose by methods based on researches carried out in this Laboratory on the constitution of mono- and disaccharides.

Prior to the study of methylated sugars initiated by Purdie and Irvine in 1901, no evidence was available regarding the particular form of glucose or of fructose present in sucrose and, in the light of later discoveries, it is not surprising that all attempts to synthesize the disaccharide by the condensation of *dextro*-rotatory glucose with *levo*-rotatory fructose resulted in failure. In 1903, however, it was shown[2] that when sucrose is methylated and the product hydrolyzed, the form of tetramethylglucose then produced is the same as that obtainable from α-methylglucoside. This result established that one half of the sucrose molecule consists of a glucose residue of normal type but, even at the time, it was evident that the fructose residue was abnormal and differed from the levorotatory form of the sugar. This was obvious from the fact that, on hydrolysis, octamethylsucrose showed no "inversion"[3] and gave a methylated fructose which, contrary to expectation, was dextrorotatory. A further important advance in the chemistry of fructose was subsequently made by Purdie and Paul,[4] who proved that two isomeric tetramethylfructoses exist, one dextro- and the other levorotatory, the reasonable conclusion being that the parent sugar would also display the same isomerism. Some years later Irvine and Robertson[5] brought forward supplementary evidence

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[1] The results described in this paper were communicated to the Institute of Chemistry (American Chemical Society) in the form of an address delivered on August 3, 1928.

[2] Purdie and Irvine, *J. Chem. Soc.*, **83**, 1036 (1903).

[3] Purdie and Irvine, *ibid.*, **87**, 1028 (1905).

[4] Purdie and Paul, *ibid.*, **91**, 289 (1907).

[5] Irvine and Robertson, *J. Chem. Soc.*, **109**, 1305 (1916).