amyl and tetra-ethoxyl. The synthesis of tin tetraphenyl by the Fittig reaction is also briefly described.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRYING, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE NON-VOLATILE ORGANIC ACIDS OF ALFALFA

BY WILLIAM A. TURNER AND ARTHUR M. HARTMAN

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In view of the ready assimilation of calcium from green or well-cured alfalfa (*Medicago Saltiva*) by dairy cows, it is desirable to learn something of the state of combination of calcium in this important roughage. As a preliminary step in this investigation it was deemed advisable to determine the nature of the organic acids occurring in alfalfa.

Euler and Bolin[1] studying the oxidizing action of a substance obtained from the juice of alfalfa leaves, "medicago-laccase," identified mesoxalic, glycolic, malic and citric acids. They were interested primarily, however, in the enzyme and did not attempt a quantitative study of the acids of alfalfa. We have investigated only the non-volatile organic acids and those not completely. We hope to give a more complete report including the volatile acids in a later communication.

Green alfalfa plants (41.25 kg.) were chopped and twice ground in a meat grinder. The pulp thus obtained weighed 35.9 kg. Fourteen liters of 4.4% hydrochloric acid was added to insure the solution of calcium salts of organic acids. The mass was then pressed in a hand press, 25.55 liters of juice being obtained. Eight liters of water was added to the press cake and the mass was pressed again, 9.56 liters more of juice being obtained. The combined press juices (including added water and acid) were then concentrated in a steam-jacketed kettle to about 5 liters of dark, tarry liquid. To about half of this liquid 2 volumes of alcohol was added. A precipitate of protein was filtered off and discarded. The acidity of the filtrate was determined by titration with 0.5 *N* alkali, and sufficient lead acetate [$Pb(C_2H_3O_2)_2.3H_2O$] to react with all the acids present was added and the mixture filtered. The filtrate was very dark in color.

The precipitate, consisting of the lead salts of organic acids as well as lead sulfate, chloride and phosphate, was washed with hot water to remove a large part of the lead chloride. The precipitate of lead salts was then treated with slightly more than sufficient sulfuric acid to precipitate the lead as sulfate, which was discarded. The sulfuric acid in the filtrate was determined by precipitation with barium chloride, and an equivalent amount of barium hydroxide was added to neutralize it. The precipitate

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[1] Euler and Bolin, *Z. physiol. Chem.*, **41**, 1 (1909).

of barium sulfate was removed and the filtrate containing free acids was evaporated on the steam-bath several times with absolute alcohol to remove water. The residue was then esterified by twice refluxing for periods of five hours with 500 cc. of absolute alcohol containing 2.5% of hydrogen chloride. The esters were extracted with ether, and washed with potassium hydroxide solution and water. After drying over sodium sulfate they were subjected to fractional distillation at 10mm. pressure.

After two distillations the following 6 fractions were obtained.

Fraction	1	2	3	4	5	6
B. p., °C.	85–90	90–100	100–116	123–135	135–165	165–168
Weight, g.	1.84	0.74	1.61	8.94	4.37	13.92

It was thought that the largest fractions, 4 and 6, probably represented fairly pure substances. They were first tested for optical activity. Fraction 4 gave a specific rotation of —10.4°, and Fraction 6 one of —0.55°. The hydrazides of the esters were prepared,[2] and their melting points were determined to be as follows: Fraction 4, 174–175°; Fraction 6, 138–142°. This would indicate that Fraction 4 is ethyl *l*-malate and Fraction 6 triethyl citrate. Ethyl *l*-malate, b. p. 128° (10 mm.);[3] specific rotation, —10.44°,[4] m. p. of hydrazide, 177.5°;[5] triethyl citrate, b. p. 185° (17 mm.[6]) optically inactive, m. p. of hydrazide 145°.[7]

If the above suppositions are correct, Fraction 5 is probably a mixture of ethyl *l*-malate and triethyl citrate.

Fraction 1 was subjected to a number of tests without any satisfactory

TABLE I

DATA ON FRACTIONS 1 AND 3

	Fraction 1	Fraction 3	Ethyl malonate
Saponification equivalent	91.2	93.2	80
Analysis, %	C 53.00[a]	52.29	52.47
	H 7.95[a]	7.92	7.56
	O 39.05	39.79	39.97
Formula	$C_7H_{13}O_4$	$C_7H_{13}O_4$	$C_7H_{12}O_4$
Hydrazide, m. p., °C.	148–149	148–150	151–152
Analysis of hydrazide, %	C 27.54		27.25
	H 5.75		6.10
	N 42.23[a]	38.88	42.42
	O 24.48		24.23

[a] Average of two determinations.

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[2] Seven-tenths g. of ester was treated with 4 cc. of absolute alcohol and 0.5 cc. of hydrazine hydrate and allowed to stand for two or three days to crystallize. The crystals were washed with ether and dried in a vacuum.

[3] Anschütz, *Ber.*, **18**, 1952 (1885).

[4] Frankland and Wharton, *J. Chem. Soc.*, **75**, 338 (1899).

[5] Curtius, *J. prakt. Chem.*, **95**, 210 (1917).

[6] Ref. 3, p. 1953.

[7] Nelson, THIS JOURNAL, **46**, 2337 (1924).

conclusion. It was finally determined to be an impure ethyl malonate, and it is quite probable that Fractions 2 and 3 contain more or less of this same ester. This conclusion is based on the data shown in Table I.

A crystallographic examination of the hydrazide crystals of Fractions 1–6 yielded the following results. Fractions 1, 2 and 3 all contained crystals of malonic dihydrazide, Fraction 2 being almost pure malonic dihydrazide as shown by comparison with a pure malonic dihydrazide prepared by us from methyl malonate. Fraction 4 could not be prepared in satisfactory crystalline condition for examination. Fractions 5 and 6 gave hydrazides containing crystals which proved to be anhydrous citric trihydrazide, that of Fraction 6 being very largely citric trihydrazide as shown by comparison with a sample of pure citric trihydrazide obtained from Mr. Nelson of the Bureau of Chemistry.

As noted by Nelson[7] there is a wide discrepancy between the melting points of his citric trihydrazide, m. p. 145°, and that prepared by Curtius, m. p. 107°. The authors undertook to discover the reason for this. Citric trihydrazide was prepared, starting with very pure citric acid and converting into triethyl citrate. The citric trihydrazide was made to crystallize by shaking thoroughly and allowing to stand overnight. Crystals of good form but different from those of Nelson's compound were obtained. They were dried at room temperature in a vacuum and found to melt at 103–104°.

Analyses of both compounds gave the following results.

Anal. Nelson's compound: C, 29.89, 29.63; H, 6.67, 6.77; N, 35.38, 35.73. Turner and Hartman's compound: C, 29.17, 28.54, 28.61; H, 5.88, 6.56, 5.99; N, 33.59, 32.50, 32.99; 34.13, 34.52.

A comparison of these with the calculated values for anhydrous citric trihydrazide and citric trihydrazide with one molecule of water of crystallization indicates that our citric trihydrazide and that of Curtius contain one molecule of water of crystallization and that Nelson's compound is anhydrous.

Calcd. for citric trihydrazide, anhydrous: C, 30.76; H, 6.03; N, 35.89. Calcd. for 1 H_2O: C, 28.56; H, 6.40; N, 33.33.

A portion of our compound dried at 70° in a vacuum lost 8.07% of its weight and melted at 149–150°. A citric trihydrazide containing one molecule of water of crystallization would contain 7.10% by weight of water. A sample of citric trihydrazide prepared from pure citric acid exactly as before, but seeded with a few crystals of Nelson's compound, produced crystals that were identical in form with those of Nelson and melted at 149–150°.

Mr. Nelson has stated in an interview with us that his original preparation of citric trihydrazide was dried in a water-jacketed oven to constant weight and that in all subsequent preparations he had seeded with a few crystals of the original preparation. The hydrazide which we prepared from alfalfa and which we identified as citric trihydrazide was seeded in this way with some of Nelson's compound, which explains the high melting point and its agreement with the value obtained by him.

Alfalfa therefore contains citric, malic and malonic acids in notable amounts, the citric being present in largest quantity, malic in about two-thirds the quantity of the citric, and malonic in about one-fourth that of the citric.

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Summary

Citric, malic and malonic acids, in notable amount, have been identified in green alfalfa plants.

BELTSVILLE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT IOWA STATE COLLEGE]

THE REACTION BETWEEN ARYL SULFONATES AND ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN, NATHANIEL J. BEABER AND CHARLES H. MYERS

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Introduction

Alkyl esters of aromatic sulfonic acids differ markedly in several respects from the corresponding esters of carboxylic acids. These differences underlie the extensive applicability of alkyl sulfonates as alkylating agents. The alkyl group of sulfonic esters can be attached directly to practically all elements commonly found in organic compounds.

Ferns and Lapworth[1] have indicated the different reactivities of the alkyl esters of sulfonic and carboxylic acids towards amines, alcoholates, phenates and the Grignard reagent in the following diagrammatic manner.

$$\mathrm{RSO_3O} \,\vdots\, \mathrm{Alkyl} \qquad\qquad \mathrm{RCO} \,\vdots\, \mathrm{O\ Alkyl}$$

The dotted lines show the place of fission when the above-mentioned reagents are used. The ready alkylating action of sulfonic esters can be correlated with that of alkyl halides, but it appears to be highly unique in the sense that no other alkyl esters of oxygen or sulfur acids behave in the same way towards certain compounds, in particular the Grignard reagents.

The reaction between alkyl esters of aromatic sulfonic acids and RMgX compounds [$2p\text{-}\mathrm{CH_3C_6H_4SO_2O\text{-}Alkyl} + 2\ \mathrm{RMgX} = 2\mathrm{R\text{-}Alkyl} + (p\text{-}\mathrm{CH_3C_6H_4SO_3})_2\mathrm{Mg} + \mathrm{MgX_2}$] permits the preparation of an unusually wide

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[1] Ferns and Lapworth, *J. Chem. Soc.*, 101, 273 (1912).