

This thiazine is very stable towards both acids and alkalies. It may be crystallized from hot, concentrated hydrochloric acid without decomposition. Prolonged boiling with concentrated alkali slowly breaks up the molecule. A boiling alkaline solution of lead acetate or mercuric oxide is without effect upon it, thus indicating the firmness with which the sulfur is held in the ring. Phenylhydrazine and aniline do not react with the compound, as may be expected now that the free aldehyde group of the monothioureide has become involved with the mercapto group in a ring closing. The action of benzenesulfochloride upon the thiazine gave, upon warming, a yellow oily mass which confirms the presence of the imino group (Hinsberg's test).

*β-Nitroacetylaminometathiazine*,  $C_4H_2O_2N_3S.(COCH_3)$ .—The *β*-nitroiminometathiazine was warmed with an excess of acetic anhydride for an hour at a temperature of about  $50^\circ$  and the solution then poured into cold water. An oil is first precipitated; this, however, by stirring and a few minutes' standing, passed over into a yellow, semi-crystalline precipitate. The product was purified by crystallization from alcohol and melted at  $141^\circ$  (cor.). It is readily soluble in alcohol, acetone, benzene, acetic ester or carbon tetrachloride; fairly soluble in ligroin or acetic acid; slightly soluble in water, but insoluble in ether.

Calculated for  $C_6H_6O_3N_3S$ : N, 21.10; S, 16.42; found, 21.24, 16.11.

This acetylaminometathiazine is a fairly stable compound. It is easily hydrolyzed, however, by boiling water and yields again the free metathiazine. The production of only a monoacetyl derivative is in exact accord with the structure of the metathiazine as already shown.

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[CONTRIBUTION FROM THE NEVADA AGRICULTURAL EXPERIMENT STATION.]

## ALFALFONE, A KETONE OF THE FORMULA $C_{21}H_{42}O$ , OBTAINED FROM ALFALFA. ALFALFA INVESTIGATION. II.

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When air-dried alfalfa meal is extracted with hot, 95% alcohol, and the extract allowed to cool, a heavy green precipitate settles out. By filtering, drying and extracting this precipitate with ether, according to the method given in my preliminary paper,<sup>1</sup> a light, fluffy powder results, which serves as the starting point for the present investigation.

About 0.5 gram of this powder together with 150 cc. nitric acid of 1.104 sp. gr. are put into a flask, connected with a reflux condenser and heated on the water bath for about two working days, or until the oily globule floating on top of the acid becomes perfectly transparent. Upon cooling the solution to the room temperature, the globule solidifies into

<sup>1</sup> THIS JOURNAL, 33, 2048.

a waxy-looking cake. The nitric acid solution is found to contain considerable quantities of oxalic acid. After pulverizing and washing the cake free from nitric acid, it is extracted with boiling acetone. The acetone solution is filtered hot, and set aside to cool, when a voluminous white precipitate appears. This precipitate is myristone and has been described in the paper to which reference has already been made.

The hot acetone, however, does not dissolve all of the powder from the oxidized fatty cake, but leaves the greater portion undissolved. This white, amorphous powder is a ketone of the formula  $C_{21}H_{42}O$ , which I have chosen to call alfalfone, since it has been obtained for the first time from alfalfa.

Alfalfone is insoluble in water, hot and cold acetone and ether, insoluble in cold alcohol but dissolves slightly when this solvent is heated to boiling. Chloroform and carbon disulphide dissolve it to some extent in the cold but easily on warming. A mixture of 90% absolute alcohol and 10% amyl alcohol dissolves alfalfone readily when hot, but precipitates it again on cooling. The same is true of a mixture of 90% petroleum ether and 10% amyl alcohol. Both of these mixtures were employed in the purification of the substance, but it was found that the melting points of the products obtained from the former solvent mixture varied somewhat with different lots and were generally lower than the melting points of the lots obtained by using the petroleum ether mixture. Two lots reprecipitated from the latter solvent mixture gave identical melting points, namely 88.5-88.8°.

Alfalfone manifests the same electrical properties as the myristone with which it is associated in alfalfa. It gives negative tests with bromine for unsaturation, with ferric chloride and alkali for phenolic character, and with acetic anhydride for hydroxyl. It does not give the characteristic color reactions for the cholesterol group. Its chloroform solution does not show any absorption bands either in the visible or ultraviolet part of the spectrum. It is neutral to litmus and phenolphthalein.

Continuous extraction of alfalfa for several months was necessary before enough of this material could be obtained to work with, as the yield is only a small fraction of one per cent. Four different lots of the unoxidized mother substance were heated with nitric acid according to the method given, separated from myristone by boiling acetone and reprecipitated two to three times from a mixture of 90% petroleum ether and 10% amyl alcohol. The resulting substances were then filtered, washed with the same solvent mixture, and dried first in the air, and then in vacuum desiccators over sulphuric acid.

These substances were burned in a Liebig furnace, giving the following results:

	Ia.	Ib.	II.	III.	IVa.	IVb.	Average.
Sub. . . .	0.1524	0.2204	0.1816	0.1696	0.1980	0.1727	...
CO <sub>2</sub> . . . .	0.4559	0.6568	0.5395	0.5038	0.5893	0.5157	...
H <sub>2</sub> O. . . .	0.1835	0.2663	0.2197	0.2018	0.2411	0.2067	...
C. . . . .	81.56	81.27	81.02	81.02	81.18	81.47	81.32
H. . . . .	13.47	13.52	13.54	13.31	13.63	13.40	13.51

Calculated for C<sub>21</sub>H<sub>42</sub>O: C, 81.20; H, 13.64.

Like myristone, this ketone did not yield an acid (at least not to any appreciable extent) when oxidized with a chromic-sulfuric acid mixture, but when it was heated with a large excess of sodium in 95% alcohol, the corresponding carbinol was obtained whose properties differ somewhat from the mother substance.

Alfalfone-carbinol is soluble in boiling acetone but settles out when the solution cools. It is more soluble in hot alcohol than the ketone. Both chloroform and amyl alcohol dissolve it at the room temperature. It goes into colloidal solution in carbon disulfide, which at once clears when the temperature is slightly raised.

The carbinol was purified by reprecipitating from hot acetone, washed and dried in a vacuum desiccator. It is a pure white, amorphous powder, with a melting point of 86.3–86.5°.

Following are the results obtained from combustions of two different lots of the carbinol:

Substance, 0.1540, 0.1859; CO<sub>2</sub>, 0.4557, 0.5499; H<sub>2</sub>O, 0.1928, 0.2254.

Calculated for C<sub>21</sub>H<sub>44</sub>O: C, 80.68 ; H, 14.20.

Found: C, 80.68, 80.68; H, 14.01 (13.57).

Not enough material was available for determining the location of the carbonyl group in the ketone or the hydroxyl in the carbinol. The cetyl ether of  $\alpha$ -hydroxy- $\beta$ -methyl butane described by Guye and Chavanne<sup>1</sup> has the same percentage composition as alfalfone-carbinol, but that they are different substances is seen from the fact that the former has a melting point of only 14°. Isoamylcetyl ether<sup>2</sup> is also isomeric with it, but since its melting point is 30° and that of the carbinol from alfalfone 86.3–86.5°, the two substances must be fundamentally different.

As the work progresses, more and more of this material will accumulate, and it is hoped that enough can be obtained so that the constitutional formula can be ascribed to this new ketone obtained from alfalfa.

<sup>1</sup> *Bull. soc. chim.*, [3] 15, 304.

<sup>2</sup> *Ann.*, 102, 220.