

that dogfish would be digested slowly in the organism, and would be capable of maintaining nitrogenous equilibrium—more capable than either beef or cod.

3. There is 0.84 per cent. urea in dogfish flesh, its presence in the blood and bile having been proved by other experimenters.

4. The dogfish, at present considered an unutilized fish, is suggested as a valuable food product.

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RICHMOND COLLEGE,  
RICHMOND, VA.

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[CONTRIBUTION FROM THE NEVADA AGRICULTURAL EXPERIMENT STATION.]

### MYRISTONE OBTAINED FROM ALFALFA.

By C. A. JACOBSON.

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Since alfalfa (or lucern) is now generally recognized as the best, all-round forage crop, being richer in nitrogen, fats and proteins than the ordinary forage crops under cultivation, it seemed of no small consequence to undertake an exhaustive study of its chemical constituents.

The variety of alfalfa employed for the present investigation was the *Medicago sativa* L. which was grown from carefully selected seed and cut in the early blooming period. After curing in the field, the hay was further dried by spreading it out on a granary floor and left for several weeks. When fully air-dried it was ground to a fine meal by passing through a feed mill used only for this purpose.

The alfalfa meal was then put into an extractor of my own construction, described elsewhere in this issue, and extracted with hot 95 per cent. alcohol for about seven hours, or until the alcohol came through colorless. The alcoholic extract was then removed from the extractor, heated to boiling on the water bath, and filtered. The filtrate was set aside to cool and then left in the ice box over night, after which the dark green precipitate, which had separated out, was filtered off and dried in the air. The resulting material, which represents 6.8 per cent. of the weight of the dry alfalfa meal, was then extracted with ether in a Soxhlet apparatus until the ether siphoned over clear, which required from 16 to 20 hours. The green ethereal extract from the Soxhlet was poured into a beaker and allowed to evaporate at the room temperature to about one-third of its original volume, when a greenish precipitate had separated out. This precipitate was then filtered and washed several times with ether on a Hirsch funnel connected with the filter pump. The

light greenish tint of the precipitate could not be washed out with this solvent, but the material itself is slightly soluble in cold ether. This faint greenish substance was dissolved in hot acetone and filtered, after which the solution was allowed to come to the temperature of the room, when the substance separated out as a fluffy voluminous precipitate which was filtered and washed with acetone, dried at first in the air and then in a desiccator over sulfuric acid.

It was first thought that the greenish tint of the material was due to impurity from the chlorophyll residues, but when it persisted, after reprecipitating the substance five times from acetone, as well as from absolute alcohol, chloroform and methyl alcohol, retaining its fairly sharp melting point of  $76.5^{\circ}$ – $77^{\circ}$  and a constant elementary composition, I concluded that this substance is a single chemical compound of considerable purity. It represents 3.4 per cent. of the green residue before extracting with ether, or only 0.23 per cent. of the dry alfalfa meal. Considerable work has already been done upon this compound, but its discussion will be postponed until some later date.

From 0.5 to 0.8 gram of this material was heated on the water bath, together with about 150 cc. of nitric acid of 1.104 sp. gr., for 12 to 15 hours, or until there was formed a perfectly clear and transparent globule, of a light yellowish color, floating around on the acid solution. Upon cooling slightly, this globule solidified into a cake of waxy appearance, which was washed with hot water until the washings no longer reacted acid. Upon evaporating the nitric acid solution at about  $50^{\circ}$ , adding water from time to time, monoclinic crystals separated out, which proved to be oxalic acid. The certainty of this is beyond question, since the crystal form, melting point, liberation of carbon monoxide with sulfuric acid, and combustion values were all confirmatory.

By titration with potassium permanganate a quantitative test showed that the weight of oxalic acid formed was 2.8 per cent. of the weight of substance subjected to oxidation, while 97.2 per cent. of the original substance was recovered unoxidized.

The waxy looking cake resulting from the nitric acid oxidation was washed free of acid, pulverized and heated together with about 300 cc. of acetone, which was kept boiling on a water bath for fifteen minutes and then filtered hot. A white insoluble residue was left in the flask, which will be described later. The acetone filtrate was set aside to cool, when a white voluminous precipitate settled out. This was reprecipitated two and three times from hot acetone, then dried in the air and finally in a desiccator over sulfuric acid. The substance obtained in this way has a pure white color, and a rather indistinct though characteristic melting point, beginning to soften at  $68^{\circ}$  and continuing more and more until a meniscus appears on the walls of the melting point tube at  $74^{\circ}$ ,

with a small nucleus remaining unmelted in the viscid liquid adhering to the sides of the tube up to 77°. 74°–75° may properly be called its melting point.

By precipitating other lots of this material from absolute alcohol, methyl alcohol and mixtures of these, the melting point was not appreciably changed. The substance obtained is undoubtedly myristone, a ketone of the formula  $(C_{13}H_{27})_2CO$ , identical with the synthetic products obtained by Krafft<sup>1</sup> and Kipping.<sup>2</sup> The latter obtained his product, having a melting point of 76°–77° from myristic acid by heating it with phosphoric anhydride.

Following are the results of combustion on two different lots of myristone from alfalfa, together with Kipping's results on the synthetic product:

	Lot 1.	Lot 2.	Kipping's synthetic $C_{27}H_{54}O$ .	Theoretical for $C_{27}H_{54}O$ .
C. ....	82.11	82.07	81.99	82.14
H. ....	13.82	13.60	13.50	13.80

Unsuccessful attempts were made to oxidize this ketone to the corresponding acid by means of chromic-sulfuric acid mixture. The secondary alcohol could be obtained, however, by reducing the ketone with a large excess of sodium in boiling 95 per cent. alcohol. The flask was connected with a reflux condenser, and the solution kept boiling for six hours, after which it was cooled and the precipitate filtered off, washed with water till free of alkali and then precipitated from 75 per cent. alcohol, washed with alcohol of the same strength containing a few drops of HCl, and finally precipitated from acetone. The carbinol thus obtained has a similar melting point to the mother substance, *i. e.*, it begins to soften slightly at 72°, gradually liquefying till a meniscus is formed at approximately 80°, but the unmelted nucleus does not become fully transparent until about 86°. 80°–81° may, however, be called its melting point.

The following table gives the result of combustions on two different lots of this substance.

	Lot 1.	Lot 2.	Kipping's synthetic $C_{27}H_{56}O$ .	Theoretical for $C_{27}H_{56}O$ .
C. ....	81.95	81.80	81.98	81.73
H. ....	13.98	14.00	14.09	14.23

From the results obtained it would seem entirely probable that this substance is the secondary alcohol of myristone, with the formula  $(C_{13}H_{27})_2CHOH$  and identical with the dimyristyl carbinol obtained by Kipping<sup>3</sup> from his synthetic ketone.

<sup>1</sup> *Ber.*, 15, 1713.

<sup>2</sup> *J. Chem. Soc.*, 63, 458.

<sup>3</sup> *Ibid.*, 63, 459.

Ceryl alcohol, having the same percentage composition, has been obtained from flax,<sup>1</sup> wool,<sup>2</sup> cocoa leaves,<sup>3</sup> etc.,<sup>4, 5</sup> but with different properties. The dimyristyl carbinol obtained from alfalfa is insoluble in water, almost wholly insoluble in cold alcohol, acetone, methyl alcohol and petroleum ether, but dissolves more or less readily when these solvents are heated. It is fairly soluble in cold chloroform and very soluble in cold amyl alcohol. The solubilities of the ketone and its carbinol do not differ greatly. When one attempts to grind the ketone in a mortar, the particles become strongly electrified and fly out, making a ring of white powder on the table surrounding the mortar.

From the foregoing discussion it would appear that myristone is found combined with another substance or substances in the plant structure of alfalfa which can be extracted with hot 95 per cent. alcohol and isolated by weak nitric acid. Work is now in progress on various other substances obtained from alfalfa.

RENO, NEVADA.

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#### NOTE.

*An Improved Extractor.*—Soon after beginning my alfalfa investigations it became apparent that the ordinary forms of extractor to be had on the market were inadequate for this work.

The alfalfa, being ground to a fine meal or powder, interfered with the siphoning arrangement in the Yocum extractor, which was then the most serviceable, and a new form had to be devised. The results are embodied in this note.

A glass tube 4 feet long and having an internal diameter of  $2\frac{1}{2}$  inches was drawn out at one end to a diameter of  $1\frac{1}{4}$  inches, the beginning of the constriction being about three inches from the end, thus making a space of about 2 inches having a uniform diameter of  $1\frac{1}{4}$  inches, and upon which a large rubber stopper is fitted, which in turn is fitted into the mouth of the distilling flask as shown in the figure. Another glass tube  $3\frac{1}{2}$  feet long having an internal diameter of 2 inches is ground at one end to fit into the small glass adapter also represented in the figure. The other end is flared and serrated so that it will just go into the large tube. The glass adapter is conical in shape, having an opening of only  $\frac{1}{4}$  inch at the lower end and provided with three glass beads fused to the outside walls, which serve to support the adapter and inside tube by engaging the constriction of the outside tube, and still leaving space

<sup>1</sup> *J. Chem. Soc.*, 57, 198.

<sup>2</sup> *Ber.*, 29, 2895.

<sup>3</sup> *Ann.*, 271, 224.

<sup>4</sup> *Ber.*, 11, 2113.

<sup>5</sup> *Z. physiol. Chem.*, 22, 409.