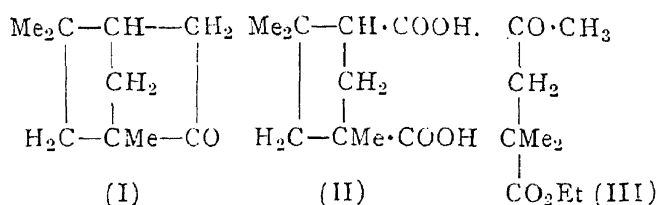
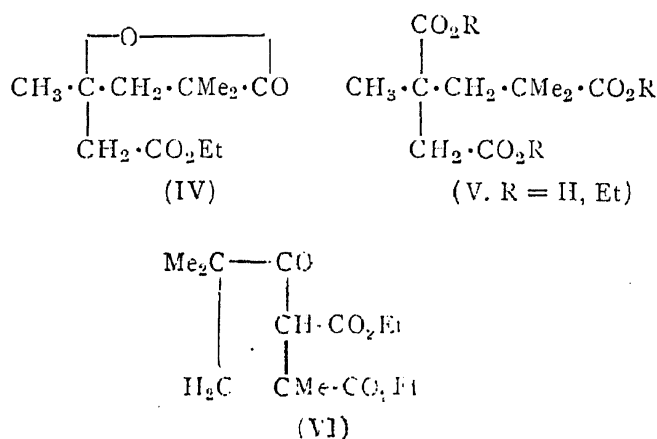


Experiments towards the Synthesis of Isufenchone and Its Degradation Products.

THE classical investigations of Wallach, Aschan and their collaborators¹ have shown the correctness of Semmler's formula for isufenchone (I). Direct evidence by synthesis, however, has been wanting for the constitution of either isufenchone or any of its products of degradation, *e.g.*, isufenchocamphoric acid (II). The present investigation has been undertaken with a view to filling such a gap, and a preliminary report is now made of the results obtained so far.



Ethylmesitonate² (III) (ethyl $\alpha\alpha$ -dimethyl lævulate), b.p. 108–110°/25 mm. (Semicarbazone, m.p. 154°; 2 : 4-dinitrophenylhydrazone, m.p. 98°) has been condensed with zinc and ethyl bromoacetate to yield the lactone of ethyl β -hydroxy- $\beta\delta\delta$ -trimethyl adipate (IV), b.p. 137–38°/6 mm. The lactonic ester adds KCN at 220° and the intermediate cyanoester yields on hydrolysis with concentrated HCl $\beta\delta$ -dimethylpentane- $\beta\delta\epsilon$ -tricarboxylic acid (V, R = H), m.p. 172°. The corresponding ester (V, R = Et) prepared by alcohol vapour method with



concentrated H₂SO₄, boils at 125–128°/1–2 mm. The constitution of the compound (VI) obtained from the ester (V) by cyclisation is being confirmed. Further work on the synthesis of isufenchone from (VI) is in progress.

My thanks are due to Prof. P. C. Guha for his interest in the work.

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¹ Wallach, *Annalen*, 1908, **362**, 191; **363**, 5.

Wallach and Homberger, *Ibid.*, 1909, **369**, 97.

Aschan, *Annalen*, 1912, **387**, 1.

Sandelin, *Ibid.*, 1913, **396**, 285.

² Pinner, *Ber.*, 1882, **15**, 529; *cf.* Anschutz and Gillet, *Annalen*, 1888, **247**, 99.

A Volumetric Method for the Estimation of Moisture.

OF the two main methods, oven drying and distillation with an entrainer, available for the determination of moisture in substances such as starch and cotton, the former is not always applicable on account of the possibility of decomposition. Thus, except for precautions in the weighing of the highly hygroscopic bone-dry cotton, the moisture content of cotton may normally be estimated by drying in an oven to constant weight, but the method is unsuitable in the case of cotton which contains certain kinds of extraneous matter or has undergone considerable degradation.

For these and other reasons the Marcusson procedure¹ of distilling the substance with a liquid such as toluene or xylene and reading the volume of the water directly has become increasingly popular. This method, however, has not been free from criticism with regard to the time involved, the choice of the entrainer and the entanglement of condensed water. According to Tate and Warren,² who have devised a new apparatus, the comparatively satisfactory types of apparatus due to Friedrichs,³ and to Bidwell and Sterling⁴ both lead to inaccurate results. A new moisture tube has also been recently described by Alexander.⁵ The extensive literature on moisture estimation apparatus would appear to point to the practical difficulties of the method, notably the removal of water drops from the inside of the condenser; as a result an "additive apparatus correction constant"⁵ seems unavoidable. A variation of the process⁶ involving the dehydration of the

distillate with anhydrous copper sulphate and assaying the increase of weight of the latter has given low values in our hands.

In the present method the distillate is led into a known volume of a standard mixture of acetic anhydride and pyridine (1 : 3); when the hydrolysis is complete, the excess acetic anhydride is converted into an equivalent amount of acetic acid and acetanilide. The whole is then made up to a convenient volume and an aliquot part titrated against alkali. If x molecules of acetic anhydride were taken and the substance contained y molecules of water, the acetic acid finally obtained is $(x + y)$ molecules; since x is known, the value of y follows. The accuracy of the method is indicated by the fact that 1 c.c. of normal caustic soda solution corresponds to 0.018 g. of water, the problem resolving itself into the estimation of acetic acid in acetic anhydride.⁷

While a water-immiscible liquid is essential for the Marcusson procedure, a solvent such as dioxane, which is miscible with water and forms an azeotropic mixture containing 20% water and boiling at 86.8°/742 mm., can be conveniently employed for the hydrolytic method. Dioxane, however, needs to be carefully purified since ethylene acetal and other impurities in technical dioxane interfere with the estimation.

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¹ Marcusson, *Mitt. aus dem Konigl. Materialprüfungssamt*, 1904, 48.

² Tate and Warren, *Analyst*, 1936, 61, 367.

³ Friedrichs, *Chem. Ztg.*, 1929, 53, 287.

⁴ Bidwell and Sterling, *J. Assoc. Off. Agric. Chem.*, 1924, 8, 295.

⁵ Alexander, *Ind. Eng. Chem. Anal. Ed.*, 1936, 8, 314.

⁶ Migray, *Ind. Eng. Chem. Anal. Ed.*, 1935, 7, 348.

⁷ Menshutkin and Wasiljew, *J. Russ. Phys. Chem. Soc.*, 1889, 21, 190; "Report of International Glycerol Commission," *Analyst*, 1911, 26, 316.

Richmond, *Analyst*, 1917, 42, 133.

Rosenbaum and Walton, *J. Amer. Chem. Soc.*, 1930, 52, 3366.

Linkage between the Blackish Purple of Sheath and Glume, and Nucellar Brown in Sorghum.

THE grains of grain sorghum are mostly naked and lack the protection of enclosed glumes. Such protection is afforded in part by the seed coats (pericarp) which may be white or coloured. The colours may be degrees of yellow, red¹ or brown.²

Some varieties of sorghum possess a nucellar layer³ just above the aleurone layer. This layer is pigmented and is of a reddish brown colour. Lying under the mesocarp which is starchy and white, this nucellar colour is masked. Nevertheless, according to the thickness of the mesocarp this underlying "vinaceous drab" (Snowden)⁴ imparts a violet tint in the white chalky grained varieties, most noticeable in the variety *feterita*. This nucellar colour is usually absent in the Indian *Durra* group of sorghums. It is present in many African sorghums and is most marked in the *caffra* sub-series of sorghum.⁴ In *Sorghum caudatum*, Stapf. it finds its best representation and expression.

Regarding the nucellar layer Snowden⁴ writes as follows:—"The colour in the grain may be confined to the outer pericarp or it may be absent there but present in the nucellar-layer, or again it may be present in both regions. In the first case the coloured part is removed by husking the grain and the colour of the flour is not affected. In the other two cases, however, the colour present in the nucellar-layer cannot readily be separated from the flour and such grains produce a dirty coloured flour which is less esteemed for some purposes, such as making cakes or bread."

Almost all the varieties with brown nucellus are borne on plants whose leaf sheaths and glumes are blackish purple. The reddish purple leaf-sheaths and glume is largely in evidence in the *Durra* group of Indian sorghums. It has been noted that in this group there is an absence of nucellar brown.

The reddish purple pigment in the leaf sheath and glume has been shown to be dominant to the blackish purple.⁵ A factor Q is present in the former and absent in the latter. In crosses between varieties having nucellar brown and those not having them, the presence of nucellar brown has proved a simple dominant to its absence.⁶ Thus a reddish purple leaf-sheath and glume