

## Hydroxy- $\beta$ -diketones from Wheat Leaf Wax

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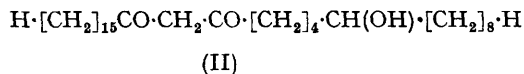
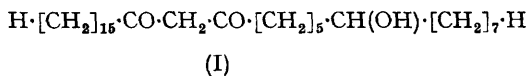
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A MIXTURE of hydroxy- $\beta$ -diketones, 8- and 9-hydroxyhentriacontane-14,16-dione (I and II) has been isolated from the leaf-surface wax of the wheat

*Triticum compactum* Host. var. Little Club. Long-chain  $\beta$ -diketones have been found in the leaf-surface waxes of a number of plants<sup>1</sup> but

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hydroxy- $\beta$ -diketones do not appear to have been isolated before.



The wax was chromatographed on a silicic acid column. Elution with (a) light petroleum gave hydrocarbons (15%), mainly nonacosane and hentriacontane; (b) solvent containing 3% ether gave esters and  $\beta$ -diketone together (40%); (c) solvent containing 10% ether gave alcohols (31%), mainly octacosanol; and finally (d) solvent containing 30% ether gave crude hydroxy- $\beta$ -diketones (19%). The unsubstituted  $\beta$ -diketones (10% of total wax) were separated from the esters as the copper complex<sup>1</sup> and shown, by the method of Horn and Lamberton,<sup>1</sup> to be mainly hentriacontane-14,16-dione.

The hydroxy- $\beta$ -diketone fraction, after purification as the copper complex, had m.p. 69.5–70.5°,  $\lambda_{\text{max}}$  273 m $\mu$  ( $\epsilon$ , 258) in EtOH. The infrared spectrum had bands at 3660 (w) and 1602 (s) cm.<sup>-1</sup> suggesting the presence of a hydroxyl group and a  $\beta$ -diketone grouping respectively. The n.m.r. spectrum (in CCl<sub>4</sub>) was in agreement with

these suggestions (CH of enolic form of  $\beta$ -diketone,  $\delta$ , 5.30; CH of CH·OH,  $\delta$  3.43; and one hydroxylic proton which was removed by D<sub>2</sub>O). The products of alkaline hydrolysis were found by gas-liquid chromatography to be: heptadecan-2-one, hydroxypentadecan-2-ones, palmitic acid, and hydroxymyristic acids. The hydroxy-acids were shown to be a mixture of approximately equal amounts of 6- and 7-hydroxymyristic acids. Chromic acid oxidation gave the monobasic acids heptanoic, caprylic, and pelargonic in the ratio 1 : 2 : 1 and the dibasic acids glutaric, adipic, and pimelic also in the ratio 1 : 2 : 1. The n.m.r. spectrum of the hydroxy-esters in quinoline, which has been found to be a much more useful solvent for comparison of hydroxy-fatty-acid esters than carbon tetrachloride,<sup>2</sup> was indistinguishable from that of a 1 : 1 mixture of synthetic methyl 6- and 7-hydroxymyristates. Mass-spectrographic analysis also confirmed that the 6- and 7-hydroxy-isomers were present (presence of 145<sup>+</sup> ion, <sup>+</sup>CH(OH)[CH<sub>2</sub>]<sub>4</sub>·CO<sub>2</sub>·CH<sub>3</sub>; and 159<sup>+</sup> ion, <sup>+</sup>CH(OH)[CH<sub>2</sub>]<sub>5</sub>·CO<sub>2</sub>·CH<sub>3</sub><sup>3</sup>).

The chain length was established by reduction<sup>1</sup> of the hydroxy- $\beta$ -diketone to n-hentriacontane, which was identified by gas-liquid chromatography. Thus the hydroxy- $\beta$ -diketone is a mixture of approximately equal amounts of (I) and (II) and has the same chain length as the simple  $\beta$ -diketone also present in the wax.

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<sup>1</sup> D. H. S. Horn and J. A. Lamberton, *Chem. and Ind.*, 1962, 2036.

<sup>2</sup> A. P. Tulloch, Unpublished work.

<sup>3</sup> R. Ryhage and E. Stenhagen, *Arkiv Kemi*, 1960, 15, 545.