Hydroxy-β-diketones from Wheat Leaf Wax

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A MIXTURE of hydroxy-β-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 β-diketones have been found in the leaf-surface waxes of a number of plants[1] but

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hydroxy-β-diketones do not appear to have been isolated before.

$$H\cdot[CH_2]_{15}\cdot CO\cdot CH_2\cdot CO\cdot[CH_2]_5\cdot CH(OH)\cdot[CH_2]_7\cdot H$$

(I)

$$H\cdot[CH_2]_{15}CO\cdot CH_2\cdot CO\cdot[CH_2]_4\cdot CH(OH)\cdot[CH_2]_8\cdot H$$

(II)

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 β-diketone together (40%); (c) solvent containing 10% ether gave alcohols (31%), mainly octacosanol; and finally (d) solvent containing 30% ether gave crude hydroxy-β-diketones (19%). The unsubstituted β-diketones (10% of total wax) were separated from the esters as the copper complex[1] and shown, by the method of Horn and Lamberton,[1] to be mainly hentriacontane-14,16-dione.

The hydroxy-β-diketone fraction, after purification as the copper complex, had m.p. 69·5—70·5°, λ_{max} 273 mμ (ε, 258) in EtOH. The infrared spectrum had bands at 3660 (w) and 1602 (s) cm.$^{-1}$ suggesting the presence of a hydroxyl group and a β-diketone grouping respectively. The n.m.r. spectrum (in CCl_4) was in agreement with these suggestions (CH of enolic form of β-diketone, δ, 5·30; CH of CH·OH, δ 3·43; and one hydroxylic proton which was removed by D_2O). 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,[2] 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^+ ion, $^+CH(OH)[CH_2]_4\cdot CO_2\cdot CH_3$; and 159^+ ion, $^+CH(OH)[CH_2]_5\cdot CO_2\cdot CH_3$[3]).

The chain length was established by reduction[1] of the hydroxy-β-diketone to n-hentriacontane, which was identified by gas–liquid chromatography. Thus the hydroxy-β-diketone is a mixture of approximately equal amounts of (I) and (II) and has the same chain length as the simple β-diketone also present in the wax.

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[1] D. H. S. Horn and J. A. Lamberton, *Chem. and Ind.*, 1962, 2036.
[2] A. P. Tulloch, Unpublished work.
[3] R. Ryhage and E. Stenhagen, *Arkiv Kemi*, 1960, **15**, 545.