Tetrahedron Letters No. 14, pp. 905-906, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE ACID-CATALYSED SELF-CONDENSATION OF 7,4'-DIHYDROXYFLAVAN

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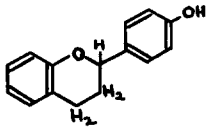
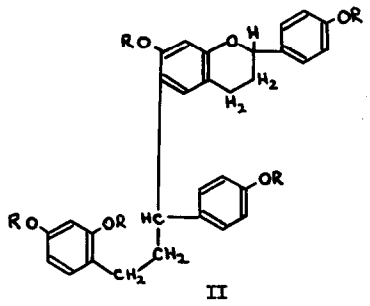
(Received 13 March 1963)

THE recent communication of Freudenberg and Weinges (1) makes it desirable for us to publish more widely some investigations on the polymerisation of flavans which we carried out in 1959 (2).

Freudenberg and Weinges did not find it possible to isolate a dimer (II, R = H) of 7,4'-dihydroxyflavan (I), since its rate of reaction to give high polymers was too great in aqueous acid. However, we found that treatment



I



II

of 7,4'-dihydroxyflavan with dry hydrogen chloride (8%) in ethanol at room temperature for 1 day gave a solution which no longer contained the dihydroxyflavan, but on Whatman No. 1 paper in 2% acetic acid at 25° two phenolic spots (diazotised sulphanilic acid spray) were detected, (A) Rf = 0.0, (B) Rf = 0.16. In n-butanol - acetic acid - water (4:1:5 v/v) the Rf values were (A) 0.85, (B) 0.775.

(1) K. Freudenberg and K. Weinges, Tetrahedron Letters, 1073 (1962).

(2) G. A. Somerfield, D. Phil. Thesis, University of Oxford (1959).

Ether extraction of the diluted reaction mixture gave a solid [λ_{max} (EtOH) 225mμ (log ε 5.68) and 286mμ (log ε 4.25)] which in 2% acetic acid was separated on a column of cellulose (Whatman No. 1, standard grade) to yield a solid (50%) of Rf 0.16, regarded as the dimer (II, R = H), and material of high molecular weight (Rf 0.0). Acetylation of (II, R = H), chromatography on alumina, and crystallisation from methanol afforded a colourless acetate (II, R = CH_3CO), m.p. 159-215° which on repeated crystallisation from methanol gave colourless prisms (5%), m.p. 200-205° (Found: C, 68.05, 67.95; H, 5.85, 5.55; M.W. (Rast), 644. $C_{40}H_{58}O_{11}$. CH_4O requires C, 67.8; H, 5.8%; $C_{40}H_{58}O_{11}$ requires M.W. 694), ν_{max} (Nujol) 3590 and 3510 cm^{-1} (weak peaks, confirming the presence of methanol of crystallisation) and 1761 cm^{-1} (very strong; acetate). Methylation of (II, R = H), chromatography on alumina, and crystallisation from ethanol yielded a colourless methoxy compound (II, R = CH_3), m.p. 135-145° (Found: C, 75.9; H, 7.3; OMe, 28.0. $C_{55}H_{58}O_6$ requires C, 75.8; H, 6.9; OMe, 28.0%). The infrared spectrum showed that methylation was complete.

It seems likely (3) that the product of the condensation is the dimer (II, R = H) since its Rf value (0.16) in 2% acetic acid is approximately half that of the monomer, 7,4'-dihydroxyflavan (Rf 0.35), and the above analyses of its acetoxy and methoxy derivatives correspond to those expected for a dimer of structure (II, R = H) in which a new phenolic hydroxyl group has been generated on condensation. The difficulty we experienced in isolating crystalline compounds probably arose from the fact that the dimer and its derivatives have two asymmetric carbon atoms and we were handling a mixture of racemates.

(3) D. J. Roux, Nature, 181, 1795 (1958).