

73. Anthoxanthins. Part XIII. Synthesis of a Colouring Matter of *Robinia pseudacacia*.

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A YELLOW colouring matter isolated from the stem-wood of *Robinia pseudacacia* by Schmid and Pietsch (*Monatsh.*, 1931, **57**, 305) has been identified as 3 : 7 : 3' : 4' : 5'-pentahydroxyflavone (I) by Schmid and Tadros (*Ber.*, 1932, **65**, 1689).

Brass and Kranz (*Annalen*, 1932, **499**, 175), employing Kostanecki's method of synthesis of flavonols, have obtained the tetramethyl ether (II; R = H, R' = Me) and, on methylation, the pentamethyl ether (II; R = R' = Me), which was found to be identical with the derivative obtained from the anthoxanthin of natural origin.



The synthesis of the colouring matter itself has been effected following the method introduced by Allan and Robinson (*J.*, 1924, **125**, 2192) and employed for the synthesis of many naturally occurring flavones and flavonols, *e.g.*, by Kalff and Robinson (*J.*, 1925, **127**, 181) in the synthesis of myricetin.

Condensation of ω -methoxyresacetophenone with trimethylgallic anhydride and sodium trimethylgallate affords, after hydrolysis of the product, the *tetramethyl* ether (II; R = Me, R' = H) and, on demethylation, the flavonol (I). The properties of the synthetic and the natural specimen and of their derivatives exhibited no divergencies; a direct comparison has been rendered possible by the courtesy of Dr. L. Schmid, who kindly sent us specimens of the natural colouring matter and of its penta-acetyl derivative.

Schmid and Tadros term the anthoxanthin 3 : 3' : 4' : 5'-tetrahydroxyflavonol and Brass and Kranz describe it as 5'-hydroxyfisetin. In view of the fact that other anthoxanthins of the flavone and flavonol classes have received special names, we venture to suggest, having regard to its botanical origin, that 3 : 7 : 3' : 4' : 5'-pentahydroxyflavone may be termed *robinetin*. This is unlikely to cause confusion with the glucoside robinin

from the same plant, because its aglucone, robigenin, has been found to be identical with kaempferol (A. G. Perkin, J., 1902, **81**, 473).

EXPERIMENTAL.

7-Hydroxy-3 : 3' : 4' : 5'-tetramethoxyflavone (II; R = Me, R' = H). A mixture of *O*-trimethylgallic anhydride (32 g.) (Kalfx and Robinson, *loc. cit.*), sodium *O*-trimethylgallate (13 g.), and ω -methoxyresacetophenone (7 g.) (Slater and Stephen, J., 1920, **117**, 312) was heated at 180–185° for 4 hr., and the melt dissolved in boiling EtOH (100 c.c.). KOH (12.5 g.) in H₂O (15 c.c.) was gradually introduced into the boiling solution, which was refluxed for $\frac{1}{2}$ hr. The EtOH was distilled under reduced press., the residue dissolved in H₂O (125 c.c.), and the filtered solution saturated with CO₂; a light brown powder (9.5 g.) then separated. This crystallised from EtOH (1 l., charcoal) in clusters of pale yellow spears (7.5 g.), m. p. 250–251°; recrystn. did not raise the m. p. (Found: C, 63.6; H, 5.1; MeO, 34.3. C₁₉H₁₈O₇ requires C, 63.7; H, 5.0; 4MeO, 34.6%). The solutions in conc. HCl and H₂SO₄ and in alkalis are yellow.

Acetyl derivative. The substance was acetylated with Ac₂O and C₅H₅N; the *product* crystallised from EtOH (charcoal) in long colourless needles, m. p. 149–150° (Found: C, 63.2; H, 5.0. C₂₁H₂₀O₈ requires C, 63.0; H, 5.0%).

3 : 7 : 3' : 4' : 5'-Pentahydroxyflavone (Robinetin) (I).—The foregoing tetramethyl ether (4 g.) was demethylated by boiling for 1 $\frac{1}{2}$ hr. in an atmosphere of CO₂ with a mixture of colourless HI aq. (60 c.c., *d* 1.7) and Ac₂O (20 c.c.); an orange hydriodide soon began to separate. After cooling, this was collected, washed with AcOH, and decomposed by boiling 50% AcOH (300 c.c.). This vol. was insufficient to effect complete solution, but the bright orange hydriodide quickly decomposed and yellow needles appeared. On cooling, the amount was greatly augmented and the substance was collected, washed with H₂O, and dried (3.2 g.). Recrystn. from 50% AcOH (500 c.c.) containing EtOH (5–10 c.c.) afforded greenish-yellow needles, which on heating became greyish-brown and then decomposed without melting at 325–330° (Found in material dried at 140° for 5 hr.: C, 59.6; H, 3.3. Calc. for C₁₅H₁₀O₇: C, 59.6; H, 3.3%). The material analysed was grey; drying at 120° does not suffice to dehydrate the crystals completely.

The synthetic colouring matter exhibited all the properties and colour reactions, including the FeCl₃ reaction, recorded by Schmid and Pietsch, and by Brass and Kranz. The characteristic colour changes in aerated alkaline solutions are best examined in buffered solutions such as those prepared from the "Universal Buffer Mixture" supplied by the British Drug Houses, Limited (cf. Robertson and Robinson, *Biochem. J.*, 1929, **23**, 35, for composition of the numbered solutions mentioned below) and direct comparison of the natural and the synthetic material showed that they exhibit identical reactions as follows. The substance does not dissolve in a solution (9) of *p*_H 8.0; it is sol. in a solution (11) of *p*_H 9.2, forming a yellow solution which goes through all the colour changes of the solution of *p*_H 10.4, but much more slowly, and after 24 hr. is pure cherry-red. In a solution (13) of *p*_H 10.4, the yellow colour rapidly changes to greenish-yellow, green, then yellow-brown, and by the end of $\frac{1}{2}$ hr. reddish-brown. During the brown stages there is an intense green fluorescence which disappears as the red colour gradually deepens; after 24 hr. the solution is cherry-red with a slight brown tinge. At no stage at this *p*_H is there any sign of a blue colour. This behaviour contrasts strongly with that in solution (15), in which the green rapidly changes through blue-green, pure blue, violet or permanganate to a brownish-red (this is the series of colour changes noted by Brass and Kranz, *loc. cit.*). With solution (17) the changes proceed very rapidly to the brownish-red stage and after 24 hr. both (15) and (17) fade to brownish-yellow.

Robinetin is a powerful mordant dye and produces shades similar to those obtained with fisetin, quercetin, and myricetin. On cotton mordanted with aluminium the shade is brownish-orange, and with iron a good black is produced, brown-olive in weak dyeings. The shades obtained with the natural and the synthetic pigment on weak and strong aluminium and iron and on a mixed mordant (brownish khaki) were identical.

O-Pentamethylrobinetin (II; R = H, R' = Me).—To a suspension of the hydroxytetramethoxyflavone (2.0 g.), described above, in acetone (50 c.c.), NaOH aq. (50 c.c. of 20%) and Me₂SO₄ (25 c.c.) were added gradually and alternately with shaking during $\frac{1}{2}$ hr. and then 25 c.c. more 20% NaOH was added and the liquid was slowly heated and finally refluxed for 20 min. The solid crystallised from MeOH (80 c.c.) in colourless rectangular prisms (1.8 g.), m. p. 149° (Found: C, 64.4; H, 5.3. Calc. for C₂₀H₂₀O₇: C, 64.5; H, 5.4%). A mixed m. p. with the pentamethyl ether formed from the natural colouring matter showed no depression.

The ether dissolves in conc. HCl to a yellow solution and an orange-yellow hydrochloride separates. This is rapidly decomposed on the addition of H₂O or EtOH.

O-Penta-acetylrobinetin.—The pentahydroxyflavone (0.6 g.) was boiled for 2 hr. with Ac₂O (25 c.c.) and 2 drops of C₅H₅N. EtOH (40 c.c.) was added to the warm solution, which was quickly filtered and, on cooling, the penta-acetate (0.75 g.) separated in cryst. threads. Recrystn. from EtOH (160 c.c.) gave a colourless product (highly electric), m. p. 223° (Found : C, 58.3; H, 4.0. Calc. for C₂₅H₂₀O₁₃ : C, 58.6; H, 3.0%). A mixed m. p. with a specimen of the penta-acetyl derivative of the natural colouring matter exhibited no depression.

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