CCCLXXVII.—*Experiments on the Synthesis of Anthocyanins. Part XI. Fisetinin Chloride.*

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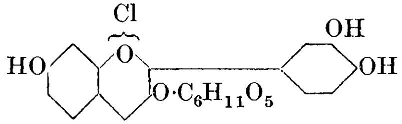
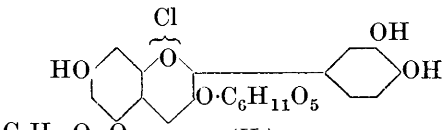
(I.)





(II.)

Employing β-resorcylaldehyde in the place of 2-*O*-benzoylphloroglucinaldehyde but otherwise following the method for the synthesis of chrysanthemin chloride (Part VI), we have obtained 3-β-glucosidylfisetinidin chloride (I). This substance has alkali-colour-reactions very similar to those of cyanin chloride and this supports the constitution (II) for the latter anthocyanin advanced in Parts VI and VII of this series. It is evident that the large effect of substitution in position 3 in cyanidin chloride is only noticeable if the hydroxyl in position 5 remains free. Substitution of the hydrogen of hydroxyls in *both* positions 3 *and* 5 has very little effect on the colour reactions in alkaline solutions.

This applies to the cyanidin, peonidin, and malvidin series but not strictly to the pelargonidin series. The 3-glucosides of the resorcinol type in all these series have been prepared and will be described in due course.

EXPERIMENTAL.

*ω-Tetra-acetyl-β-glucosidoxy-*3 : 4-*diacetoxyacetophenone.*—The preparation of the glucoside was carried out under the following conditions. The carbinol (2 g.) and tetra-acetylglucosidyl bromide (5 g.) in dry benzene (20 c.c.) were heated to 40° and silver carbonate (6 g.) was added. The temperature was maintained at 50—60° for 45 minutes and then at 80° for 15 minutes. The glucoside ultimately isolated weighed 1·65 g.

Fisetinin Picrate.—A solution of β-resorcylaldehyde (0·7 g.) and ω-tetra-acetyl-β-glucosidoxydiacetoxyacetophenone (1·94 g.) in ethyl acetate (*ca.* 10 c.c.) was saturated with hydrogen chloride at 0°, all the materials having been thoroughly dried. After the gas had been passed for 3 hours, the solution was kept for 36 hours in the ice-chest; it was then filtered, and the flavylium salt precipitated by means of ether (yield, 1·63 g.). The crude chloride (6 g.) was finely powdered and added to 8% sodium hydroxide solution (144 c.c.) at 10° under hydrogen, and the mixture kept for 3 hours at room temperature. Hydrochloric acid (260 c.c. of 7%) was then added to the reddish-brown solution, which became clear deep red and was heated at 60° in order to complete the formation of the flavylium salt. The *picrate*, precipitated by the addition of saturated aqueous picric acid (400 c.c.), was crystallised by the addition of saturated aqueous picric acid to its solution in hot methyl alcohol, clusters of flat red needles (4·2 g.) being obtained after two crystallisations (Found in air-dried material: C, 42·9; H, 4·2; N, 5·7. Found in material dried at 105° in a vacuum: C, 49·0; H, 3·8; N, 6·1. $C_{27}H_{23}O_{17}N_3,5H_2O$ requires C, 43·3; H, 4·4; N, 5·6%. $C_{27}H_{23}O_{17}N_3$ requires C, 49·1; H, 3·5; N, 6·4%).

Fisetinin Chloride.—The picrate was converted into chloride in the usual manner by solution in methyl-alcoholic hydrogen chloride and precipitation with ether. The crude salt crystallised on trituration with 5% ethyl-alcoholic hydrogen chloride and was recrystallised from 3% ethyl-alcoholic hydrogen chloride. It separated in short, slender, microscopic needles, often forming dense clusters. The mass was dark brown-green with a weak lustre

(Found in an air-dried specimen : C, 51·0 ; H, 4·9 ; Cl, 7·2 ; loss at 110° in a high vacuum, 3·3, 3·2. Found in dried material: C, 53·1 ; H, 4·9 ; Cl, 7·4. $C_{21}H_{21}O_{10}Cl,1·5H_2O$ requires C, 50·9 ; H, 4·9 ; Cl, 7·2 ; $1H_2O$, 3·7%. $C_{21}H_{21}O_{10}Cl,0·5H_2O$ requires C, 52·8 ; H, 4·6 ; Cl, 7·4%).

Fisetinin chloride is generally similar to chrysanthemin in its properties, but its solutions in dilute hydrochloric acid have a more orange-red tinge. It has a higher distribution number than chrysanthemin : this and other properties will be recorded later. It dissolves in aqueous sodium carbonate to a royal-blue solution, pure blue on dilution; addition of sodium hydroxide produces no change in the blue shade but soon destroys the colour, leaving a brown-green, yellow, or colourless solution according to the concentration.

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