

PIGMENTS OF COTTON FLOWERS

Part VI.* Methylation of Herbacetin

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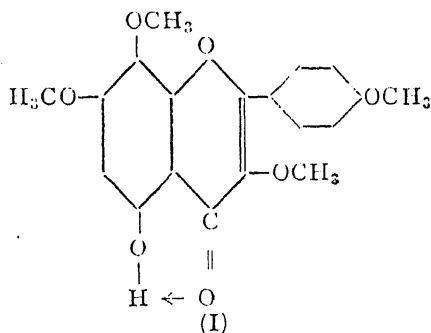
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HERBACETIN is a new flavonol which was isolated as its glucoside from the Indian cotton flowers¹ by Neelakantam and Seshadri who also established its constitution² as 3:5:7:8:4'-pentahydroxyflavone. It has been synthesised by Goldsworthy and Robinson.³ The methylation of this substance by the ordinary methods using dimethyl sulphate or methyl iodide is difficult since it undergoes oxidation very readily in the presence of alkali and air. With diazomethane it is not completely methylated; only a tetramethyl ether is formed which crystallises as a hydrate and loses the water of crystallisation (2 molecules) at about 120°. It is here described as 3:7:8:4'-tetramethylherbacetin since it is well known that position 5 is left unaffected by diazomethane. It is different from the isomeric ether, 3:5:8:4'-tetramethylherbacetin prepared by Goldsworthy and Robinson³ in the course of their synthesis of herbacetin. The melting points and colour reactions are quite different. It is noteworthy that in the partially methylated flavonols a free hydroxyl group in position 5 does not markedly raise the melting point as compared with the completely methylated ethers whereas a free hydroxyl group in position 7 invariably raises the melting point considerably. This is obviously due to the effect of chelation between the carbonyl and the hydroxyl in the fifth position as in (I). The same effect accounts for the resistance to methylation offered by this position.



* The paper entitled "Constitution of Gossypitrin" published in this Journal, 1937, 6, 12, is considered as Part V of this series.

Further methylation of 3 : 7 : 8 : 4'-tetramethylherbacetin with dimethyl sulphate and sodium hydroxide in aqueous acetone solution (Baker and Robinson's method⁴) yields pentamethylherbacetin. This compound also, like the tetramethyl ether, crystallises as a hydrate (3 molecules of water) and becomes anhydrous on drying at about 120°. In its reactions however it differs markedly from the tetramethylherbacetin. The anhydrous compound resembles closely in all its properties the sample of pentamethyl herbacetin obtained by Goldsworthy and Robinson by methylating 3 : 5 : 8 : 4'-tetramethylherbacetin with dimethyl sulphate and sodium hydroxide.

Experimental

3 : 7 : 8 : 4'-*Tetramethylherbacetin*.—Herbacetin (100 mg.) was dissolved in anhydrous methyl alcohol (25 c.c.) and treated at the room temperature (25°) with an ethereal solution of diazomethane (1 g.) in small quantities at a time. The solution became cherry red and the colour gradually disappeared. After leaving overnight, the ether was removed on a water-bath and more methyl alcohol was added. The liquid was then treated again with an ethereal solution of diazomethane (1 g.) in the above manner. After leaving overnight, the alcohol and ether were removed completely on a water-bath. On adding a few drops of water, a yellow sticky solid separated out. It was purified by crystallisation from aqueous alcohol twice (using a little animal charcoal) and finally from acetic acid. The tetramethyl ether was then obtained as yellow narrow rectangular plates which shrank and sintered from 120° to 125° (dehydration) and melted completely at 159–60°. (Found: Loss of H₂O, 9.0; C, 58.1; H, 5.8; OCH₃, 31.6; C₁₉H₁₈O₇, 2H₂O requires loss of H₂O, 9.1; C, 57.9; H, 5.6; OCH₃, 31.5%.) The substance easily lost all the water of crystallisation when kept at 120° for about two hours. The dehydrated sample melted at 160–62°. The hydrate lost one and a half molecules of water, when left in a vacuum desiccator for a day and the product contained only half a molecule of water. (Found: Loss of H₂O, 2.4; C₁₉H₁₈O₇, $\frac{1}{2}$ H₂O requires loss of H₂O, 2.5%.) The substance dissolved in concentrated hydrochloric acid or sodium hydroxide forming a yellow solution. Ferric chloride imparted a beautiful green colour to the substance in alcoholic solution.

3 : 5 : 7 : 8 : 4'-*Pentamethylherbacetin*.—The tetramethyl compound (I) (50 mg.) was dissolved in 10 c.c. of acetone. Dimethyl sulphate (1 c.c.) and 20% aqueous sodium hydroxide (1 c.c.) were added to the solution. An orange colour developed immediately and faded away gradually on shaking. Further quantities of dimethyl sulphate (2.5 c.c.) and sodium hydroxide (2.5 c.c.) were added in small quantities alternately and the contents were

shaken vigorously after each addition. Subsequently the liquid was kept strongly alkaline by the gradual addition of 3 c.c. more of the 20% alkali. The contents were left overnight and then refluxed on a water-bath for an hour. The acetone present was then driven off on the water-bath. On cooling and diluting the liquid, a colourless fibrous solid separated out. It could be easily crystallised from aqueous alcohol using a little animal charcoal in the form of fibrous needles. The pentamethyl ether sintered from 98 to 100° (dehydration) and melted at 156–58°. This could be completely dehydrated at 120° as in the case of the tetramethyl ether. (Found: Loss of H₂O, 12.5; C₂₀H₂₀O₇, 3H₂O requires loss of H₂O, 12.8%.) The dehydrated specimen melted at 157–58° (Goldsworthy and Robinson gave the melting point as 156–58°) and the mixed melting point with the dehydrated tetramethyl ether was depressed and indefinite from 140 to 45°. (Found: in the dehydrated specimen OCH₃, 41.4; C₂₀H₂₀O₇ requires OCH₃, 41.7%.) As stated by the above authors, the substance dissolved in cold concentrated or hot dilute hydrochloric acid forming a yellow solution of the oxonium salt, produced crystalline precipitates with ferric chloride and platinic chloride solutions and adsorbed iodine from aqueous solutions.

Summary

The action of diazomethane on herbacetin yields 3:7:8:4'-tetramethylherbacetin. The pentamethyl ether is obtained by the further methylation of the above tetramethyl compound with dimethyl sulphate and sodium hydroxide in aqueous acetone medium.

REFERENCES

1. Neelakantam, Seshadri and Rao *Proc. Ind. Acad. Sci. (A)*, 1935, **2**, 491.
2. Neelakantam and Seshadri *Ibid.*, 1937, **4**, 357.
3. Goldsworthy and Robinson *J.C.S.*, 1938, **58**.
4. Baker and Robinson *Ibid.*, 1928, 3117.