

# A NOTE ON THE CONSTITUTION OF GOSSYPITRIN

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IN the study of the constitution of this glucoside there was originally difficulty in methylating it. It is very sensitive to alkali and undergoes decomposition. Diazo-methane effected only partial methylation,<sup>1</sup> the resistant 5-hydroxyl group being left out. However, methylation of the acetate using dimethyl sulphate and potash in aqueous acetone solution led to successful results.<sup>2</sup> The glucoside methyl ether was isolated and hydrolysed and the product identified as 3:5:8:3':4'-*O*-pentamethyl-gossypetin having a free hydroxyl in the 7-position, thus showing that gossypitrin is a 7-glucoside. Subsequently other methods of methylation have been examined in this laboratory. Methyl iodide and anhydrous potassium carbonate in dry acetone medium do not bring about complete methylation in the gossypetin series of flavonols.<sup>3</sup> On the other hand, the use of dimethyl sulphate has led to the desired results and the method is quite convenient and economical. Though gossypitrin is sparingly soluble in dry acetone, a fine suspension of it reacts with dimethyl sulphate and the fully methylated product is obtained in good yield.

In the earlier publication the melting point of the gossypitrin methyl ether was wrongly reported as 290°. The correct melting point is 177-78°. The same product is obtained by the methylation of the acetate as already described and by the direct methylation of the glucoside as now carried out. Originally the identification of the pentamethyl gossypetin was made by a comparison of its properties with the description given by Baker, Nodzu and Robinson<sup>4</sup> for their synthetic sample. It has now been possible to make this compound synthetically again for direct comparison and mixed melting point. Since in the study of partial methyl ethers of flavones and flavonols the ethyl ethers have been found to be useful derivatives, the 7-ethyl ether of *O*-pentamethyl gossypetin has also now been made and described.

## EXPERIMENTAL

### *Methylation of Gossypitrin*

Finely powdered gossypitrin (1.0 g.) was suspended in dry acetone (25 c.c.) and redistilled dimethyl sulphate (5 c.c.) and anhydrous potassium carbonate (6 g.) added. The mixture was refluxed for 30 hours on a water-bath, filtered and the inorganic salts washed with warm acetone. Distillation

of the solvent from the filtrate yielded a sticky red solid which crystallised from alcohol as almost colourless prisms; it slowly developed a yellow colour on exposure to air. It melted at 179–80°, did not dissolve in alkali and did not give any colour with alcoholic ferric chloride.

Methyl gossypitrin was also prepared by the method of Rao and Seshadri<sup>2</sup> and recrystallised from glacial acetic acid. It melted at 179–80° and did not depress the melting point of the sample described above.

Methyl gossypitrin was hydrolysed by boiling with 7% aqueous alcoholic (1 : 1) sulphuric acid for 2 hours. The product (pentamethyl gossypetin) crystallised from dilute alcohol as rectangular prisms melting at 250–1°. It was soluble in alkali and did not give any colour with ferric chloride. It was acetylated in the usual way with acetic anhydride and sodium acetate. The product crystallised from ethyl acetate as colourless prisms melting at 169–70°. It was insoluble in alkali and easily soluble in alcohol and ethyl acetate.

The pentamethyl gossypetin and its acetate were identical with synthetic samples of 3 : 5 : 8 : 3' : 4'-pentamethoxy-7-hydroxy flavone and its acetate and the mixed melting points were undepressed. The ketone intermediate required for this synthesis was made by the simplified process recently reported.<sup>5</sup>

The pentamethyl gossypetin (0.2 g.) was ethylated by boiling with excess of ethyl iodide (0.5 c.c.) and ignited potassium carbonate (2 g.) in anhydrous acetone medium for 6 hours. The 7-ethyl ether crystallised from rectified spirit as pale yellow small prisms melting at 170°. It was insoluble in alkali and did not give any colour with ferric chloride. On reduction with magnesium and hydrochloric acid, a red colour was developed rapidly. (Found: C, 60.7; H, 5.9; loss on drying 3.8; C<sub>22</sub>H<sub>24</sub>O<sub>8</sub>, H<sub>2</sub>O requires C, 60.8; H, 6.0; H<sub>2</sub>O, 4.1%.)

#### SUMMARY

Gossypitrin is fully methylated by means of dimethyl sulphate and potassium carbonate in acetone medium. The pentamethyl gossypetin obtained by hydrolysis has been directly compared with a synthetic sample and mixed melting point taken. Its ethyl ether has also been made.

#### REFERENCES

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2. Rao and Seshadri .. *Ibid.*, A, 1939, 9, 177.
3. Rao, Reddy and Seshadri .. *Ibid.*, A, 1940, 12, 495.
4. Baker, Nodzu and Robinson .. *J. C. S.*, 1929, 74.
5. Rao, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1944, 19, 88.