

A NOTE ON THE METHYLATION OF QUERCETAGETIN

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THE methylation of the hexahydroxy flavone, quercetagetin with methyl iodide and potash was first carried out by Perkin.¹ Though an excess of the reagents was used, the main product was the pentamethyl ether, and the completely methylated substance was obtained in very small amounts. As an alternative method for the preparation of the hexamethyl ether, Perkin subjected the dry potassium salt of the pentamethyl compound to the action of dimethyl sulphate, but the yield was poor even then. The pentamethyl ether (3:6:7:3':4'-) was subsequently prepared by Baker, Nodzu and Robinson² during the course of the synthesis of quercetagetin. These authors could effect further methylation of the pentamethyl ether very satisfactorily by treating the compound in acetone solution with dimethyl sulphate and alkali.

It has now been found that the hexamethyl ether can be readily prepared in a very satisfactory yield (about 90%) according to the method of Rao and Seshadri.³ The acetyl derivative was dissolved in acetone and the solution treated with the requisite amounts of dimethyl sulphate and 20% sodium hydroxide alternately in small amounts. Finally the medium was made definitely alkaline by the addition of further quantities of the alkali. After leaving overnight the acetone was removed by heating on a water-bath, and when the remaining alkaline solution was acidified, the hexamethyl ether was produced. After crystallisation from alcohol using a little animal charcoal, the substance was obtained as narrow rectangular plates melting at 142-44°. Mahal⁴ followed a similar method with slight alterations but the yield was recorded to be only 33% on the weight of the acetate taken.

The action of diazomethane on quercetagetin does not seem to have been studied before. An anhydrous methyl alcohol or dioxan solution of the flavonol was treated with excess of diazomethane in ethereal solution, adding the latter in small quantities during two days. After evaporating off the solvent, a brown oily liquid was obtained, which solidified on adding a little

water and keeping in the ice-chest for some time. The brown solid was purified by crystallisation from alcohol using a little animal charcoal. Hexamethyl quercetagenin melting at 142–44° was obtained in a yield of 80%.

The action of methyl iodide and anhydrous potassium carbonate has recently been studied in our laboratories on some of the flavonols, herbacetin, gossypetin and quercetin, and their action has been found to be similar to that of diazomethane.⁵ A deviation has been noticed in the case of quercetagenin. When a solution of the flavonol in dry acetone was treated with anhydrous potassium carbonate, the pigment got precipitated almost completely, and the subsequent boiling of the mixture with methyl iodide for 60 hours did not bring about any methylation, the original substance being recovered unchanged. The experiment was repeated using a mixture of dioxan and dry acetone to dissolve the pigment. Even now the flavonol got precipitated on adding anhydrous potassium carbonate; but on boiling with methyl iodide a pale yellow substance began to float over the surface of the liquid. It was mechanically separated out and crystallised from alcohol, when it appeared as almost colourless rectangular plates melting at 160–61°. It was found to be identical with 3:6:7:3':4'-pentamethyl quercetagenin, developing a brown colour with a trace of ferric chloride and giving a dull olive-green with an excess. The yield too was poor.

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REFERENCES

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