

# SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

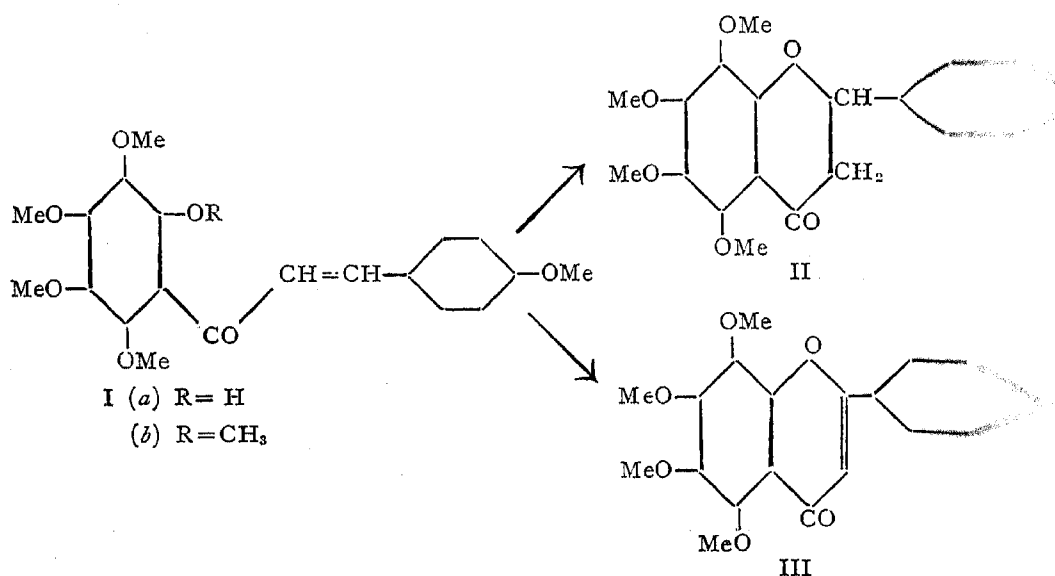
## Part LVII. Synthesis of 5:6:7:8:4'-Pentamethoxy Flavanone and The Constitution of Ponkanetin

BY J. M. SEHGAL, T. R. SESHADRI, F.A.Sc. AND K. L. VADEHARI  
(Department of Chemistry, University of Delhi, Delhi)

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ICHIKAWA and YAMASHITA<sup>1</sup> reported the isolation of a new flavanone derivative melting at 152° from the peels of *Citrus poonensis* Hort. ponkanetin and gave it the constitution of 5:6:7:8:4'-pentamethoxy flavanone (II) as a result of detailed degradation study. The constitution of this constitution has now been synthesised and is found to have a melting point (108-09°). 5:6:7:8-Tetramethoxy flavanone has been made earlier by Rao, Rao and Seshadri<sup>2</sup> was recorded to melt at 110°. The higher member is, therefore, more likely to have a melting point rather than 152°. Hence the structure assigned to ponkanetin may require reconsideration.

For the synthesis of the pentamethoxy flavanone (II), 3:4:5:6:4'-pentamethoxy chalcone (Ia) is the intermediate. A yield of it is obtained by the condensation of pentamethoxy benzoyl *p*-methoxy cinnamoyl chloride<sup>4</sup> in dry ether medium in the presence of aluminium chloride. The use of nitrobenzene reduces the yield considerably.



On treatment with alcoholic acid it smoothly undergoes isomeric change to 5:6:7:8:4'-pentamethoxy flavanone (II). It is also converted into the known 5:6:7:8:4'-pentamethoxy flavone (III)<sup>5</sup> by oxidation with selenium dioxide.

## EXPERIMENTAL

*2-Hydroxy-3:4:5:6:4'-pentamethoxy chalkone (I a)*.—Anhydrous aluminium chloride (10 g.) was dissolved in absolute ether (100 c.c.) with cooling in water and pentamethoxy benzene (5 g.) added. To the mixture which was cooled in water, a solution of *p*-methoxy cinnamoyl chloride (5.5 g.) in ether (50 c.c.) was slowly added during the course of 30 minutes with stirring. During this time, the dark coloured aluminium chloride complex of the chalkone began to separate. After standing overnight, the solvent was distilled off and to the residue was cautiously added water (200 c.c.) and concentrated hydrochloric acid (25 c.c.) and the mixture heated on a water-bath for five minutes. It was then cooled and extracted with ether (3 × 150 c.c.), the ether extract washed with dilute hydrochloric acid and shaken with excess of 10% aqueous sodium hydroxide. Acidification of the aqueous solution precipitated an oil which gradually solidified to an orange coloured mass on leaving it overnight in the refrigerator. It crystallised from petroleum ether as small orange yellow prisms and needles melting at 91–92°; 2.7 g. (Found: C, 63.8; H, 5.9; C<sub>20</sub>H<sub>22</sub>O<sub>7</sub> requires C, 64.2; H, 5.9%). It was easily soluble in common organic solvents and gave a brownish red colour with alcoholic ferric chloride. *2:3:4:5:6:4'-Hexamethoxy chalkone (I b)*, obtained by methylation with dimethyl sulphate and potassium carbonate in acetone medium, crystallised from petroleum ether as pale straw coloured long rhombohedral tablets; m.p. 105–06°; (Found: C, 65.4; H, 6.5; C<sub>21</sub>H<sub>24</sub>O<sub>7</sub> requires C, 64.9; H, 6.2%). The compound gave no colour with alcoholic ferric chloride.

*5:6:7:8:4'-Pentamethoxy flavanone (II)*.—A solution of the above hydroxy chalkone (*I a*) (2 g.) in alcohol (100 c.c.) was treated with concentrated sulphuric acid (2.2 c.c.) and the resulting solution was refluxed for 30 hours in a water-bath. It was then diluted with water (100 c.c.) and distilled to remove most of the alcohol, the product taken up in a large excess of ether (400 c.c.) and the ether solution washed several times with cold aqueous 2% sodium hydroxide, dried and the ether distilled off. The residue left behind, crystallised from dry ether as colourless large flat needles and long rectangular plates melting at 108–09°; 1.2 g. (Found: C, 64.6; H, 5.4; C<sub>20</sub>H<sub>22</sub>O<sub>7</sub> requires C, 64.2; H, 5.9%). The compound developed a deep pink colour with magnesium and hydrochloric acid and with concentrated

nitric acid a deep orange red. It gave no colour with alcoholic ferric chloride.

5:6:7:8:4'-Pentamethoxy flavone (III).—The above chalcone (I a) (2 g.) was refluxed with selenium dioxide (1 g.) in amyl alcohol (25 c.c.) for 40 hours in an oil-bath at 140–45°. The insoluble mass was filtered off and the alcohol removed by steam distillation. The residue left behind solidified on leaving it in the refrigerator. It crystallised from ethyl acetate-petroleum ether mixture as long rectangular prisms and rods melting at 150–51°; 0.8 g. (Found: C, 63.9; H, 5.4;  $C_{20}H_{20}O_7$  requires C, 64.5; H, 5.4%). Murti, Rao and Seshadri<sup>5</sup> who prepared it by a different route also reported the same melting point.

#### SUMMARY

5:6:7:8:4'-Pentamethoxy flavanone has been synthesised. The product is different from ponkanetin which was given the above structure earlier by Ichikawa and Yamashita.

#### REFERENCES

1. Ichikawa and Yamashita .. *J. Chem. Soc. Japan*, 1941, **62**, 1006.
2. Rao, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1948, **28 A**, 201.
3. Baker .. *J. Chem. Soc.*, 1941, 666.
4. Perkin .. *Ibid.*, 1877, 410.
5. Murti, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1947, **26 A**, 186.