

hydroxyl in the fused benzene ring. The treatment of calycopterin with aluminium chloride has resulted in a new flavone, which exhibits the usual properties of a catechol derivative, *e.g.*, the characteristic red-brown colouration with ammonium molybdate and acetic acid,⁶ and must therefore be 5 : 6 : 4'-trihydroxy-3 : 7 : 8-trimethoxyflavone (VII) or 3 : 5 : 6 : 4'-tetrahydroxy-7 : 8-dimethoxyflavone (VIII); the second alternative needs to be considered since we have noticed that a 3-methoxyl is also susceptible to demethylation by aluminium chloride. The second hydroxyl in calycopterin being in the 6-position, calycopterin may now be formulated as 6 : 4'-dihydroxy-3 : 5 : 7 : 8-tetramethoxyflavone (IX).

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¹ Ratnagiriswaran, Sehra and Venkataraman, *Biochem. J.*, 1934, **28**, 1964.

² Karrer, *Helv. Chim. Acta*, 1934, **17**, 1560.

³ Karrer and Venkataraman, *Nature*, 1935, **135**, 878.

⁴ Compare also Bharadwaj and Venkataraman, *Curr. Sci.*, 1933, **2**, 50.

⁵ Mahal, Rai and Venkataraman. *J. Chem. Soc.*, 1935, p. 866.

⁶ Quastel, *Analyst*, 1931, **56**, 311.

Condensation of ω -Bromoacetophenone with 1-*o*-Aminophenyl-3-Phenylthiocarbamide.

THE condensation of ω -bromoacetophenone with 1-*o*-aminophenyl-3-phenylthiocarbamide yielded a compound (m.p. 230° decomp.; empirical formula $C_{15}H_{13}ON_2SBr$) to which a heptathiodiazine structure was assigned by me.¹ Pathak² has obtained, by carrying out the same condensation, a compound (m.p. 223° decomp.) possessing the same empirical formula and finds that it is the hydrobromide of a weak heterocyclic base. These two compounds have been regarded by him as identical.

That the compound (m.p. 230° decomp.) isolated by me is not the hydrobromide of a heterocyclic base but possesses the heptathiodiazine structure is definitely proved by the fact that it is, as already mentioned in my original paper, acidic in nature being soluble in cold dilute alkali and precipitated by acids. This property, *viz.*, that the compound is unaffected by sodium bicarbonate solution and is precipitated *unchanged* by acid from its solution in alkali, has been

again established and dispels any idea of the compound being a hydrobromide. The compound melts with decomposition to form a dark brown viscous liquid which emits smell of ω -bromoacetophenone.

In view of the properties of my compound as mentioned in my original paper, it is really surprising how Pathak could regard the two compounds as identical, and his conclusion seems not to be well founded. From Pathak's observations, it seems very probable that his compound is entirely different from mine and slight difference in experimental conditions employed by him may account for the formation of a different compound.

My compound (m.p. 230° decomp.) can be prepared as follows: An intimate mixture of the reactants (equimolecular proportions) is mixed, at ordinary temperature, with glacial acetic acid and shaken, when a clear solution is obtained accompanied by rise in temperature. In about an hour a solid is precipitated which after precipitation from an alkaline solution by acid is crystallised twice from glacial acetic acid in colourless needles.

Pathak's further observation by way of comparing the chemical characteristics of both the compounds seems to be desirable.

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¹ T. N. Ghosh *J. Indian Chem. Soc.*, 1931, **8**, 71.

² Pathak, *J. Indian Chem. Soc.*, 1935, **12**, 463.

Synthesis of "Ketonopinone" (4 : 6-Diketonopinane).

THE synthesis of pinononic acid (III) and its methyl ester (I) starting from *cis*-norpinic anhydride has been reported by us.¹ The conversion of (I) into ketonopinone (II) has now been effected by means of sodium in toluene or sodium methoxide in alcohol solution. Ketonopinone (II), m.p. 104°, purified through its copper derivative (sint 238°) gives a violet coloration with $FeCl_3$, dissolves in sodium bicarbonate, decolourises alkaline permanganate and absorbs bromine in chloroform solution. The constitution was confirmed by hydrolysing it with baryta to pinononic acid (III). Reduction of this diketone to nopinone and nopinane is in progress,