

# COLOURING MATTER OF TAMBUL SEEDS

## Part V. Synthesis of 7:8:4'-O-trimethyl-herbacetin considered to be identical with tambulin

BY K. J. BALAKRISHNA AND T. R. SESHADRI, F.A.Sc.

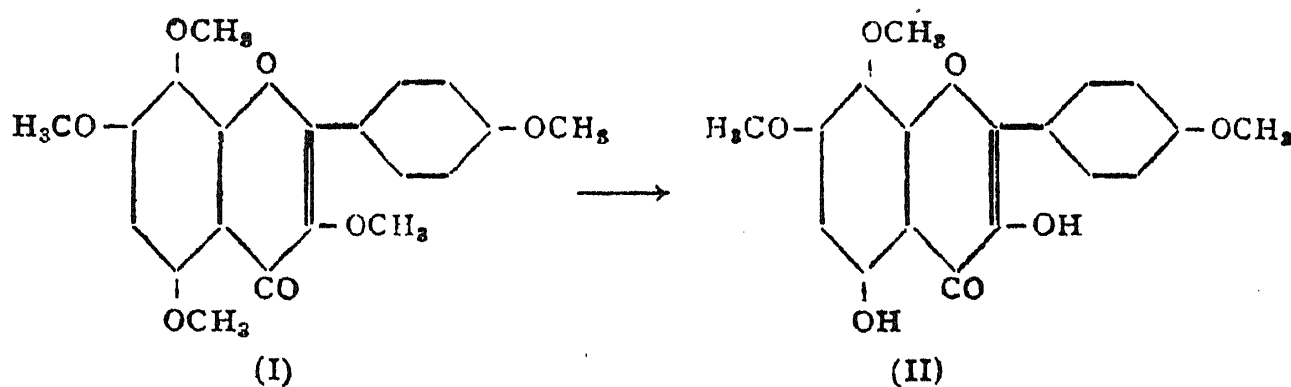
(From the Department of Chemistry, Andhra University, Waltair)

Received August 14, 1947

BOSE AND BOSE<sup>1</sup> who isolated tambulin from tambul seeds proposed for it the constitution of 3:8:4'-O-trimethyl-herbacetin. A substance of this constitution could be synthesised easily using the method of nuclear oxidation in flavones; its properties were described by Balakrishna and Seshadri in Part III.<sup>2</sup> It differed from tambulin markedly; its melting point was much higher and its colour less bright. It was felt that the melting point of tambulin was too low for the proposed structure. No sample of tambulin was available for further examination. However, an analysis of the evidences adduced by Bose and Bose suggested other possibilities. The isolation of anisic acid as a product of alkali fission fixed a methyl ether group in the 4'-position. From analogy with tambuletin and also from the colour reactions of tambulin the location of a second methoxyl in the 8-position seemed to be definite. Bose and Bose considered that the third methoxyl was in the 3-position because the compound was stable to aëreal oxidation in alkaline solution. From our experience this could not be supported. It has been found that kempferol is considerably stable and could be separated from accompanying herbacetin by using this property.<sup>3</sup> Galangin is similarly stable. Instability does not seem to depend only on the presence of a 3-hydroxyl group, but also on the number and location of other hydroxyl groups in the molecule. Based on this point and on the observation that tambulin is different from 3:8:4'-O-trimethyl-herbacetin, the alternative of 7:8:4'-O-trimethyl herbacetin structure was considered to be more probable. The melting point of a compound of this structure was expected to agree with that of tambulin.

Among the possible methods for the synthesis of the required 7:8:4'-O-trimethyl herbacetin (II) partial demethylation of the pentamethyl ether of herbacetin using anhydrous aluminium chloride in nitrobenzene solution appeared to be the most convenient. This method of simultaneous hydrolysis of 3- and 5- methoxyl groups has been adopted successfully in a number of analogous cases and the synthesis of partial methyl ethers of galangin,

kæmpferol and quercetin reported recently.<sup>4</sup> The reaction proceeds smoothly with O-pentamethyl herbacetin and the product (II) is found to have all the properties given in the literature for tambulin. Though unfortunately the original sample of tambulin is not available for direct comparison and the determination of the mixed melting point and extraordinarily it could not be isolated in the course of our examination of the tambul seeds, the agreement in properties is so close that the constitution of tambulin may be considered to have been established.



#### EXPERIMENTAL

7-Hydroxy-5 : 8 : 3 : 4'-tetramethoxy-flavone was prepared according to the method of Goldsworthy and Robinson<sup>5</sup> by condensing 2 : 4-dihydroxy- $\omega$ -3 : 6-trimethoxy-acetophenone (1.0 g.) with anisic anhydride (10 g.) and sodium anisate (4.0 g.). The 7-hydroxy-compound was methylated in dry acetone solution using anhydrous potassium carbonate and dimethyl sulphate and pentamethyl herbacetin (I) (0.8 g.) melting at 156–58° was obtained.

#### 3 : 5-Dihydroxy-7 : 8 : 4'-trimethoxy flavone (II)

To a solution of the pentamethyl ether of herbacetin (I) (0.8 g.) in dry nitrobenzene (8 c.c.) a suspension of anhydrous aluminium chloride (1.6 g.) in the same solvent (8 c.c.) was added. The mixture was heated at 100° over a boiling water-bath for one hour. After cooling the solution, petroleum ether was added when a greenish-black solid (aluminium chloride complex) separated out. It was filtered and washed free from nitrobenzene with more petroleum ether. It was then added in small quantities to ice-cold dilute hydrochloric acid. After setting aside for an hour, the yellow compound that separated out was filtered and washed free from acid. It was first crystallised from alcohol and then from a mixture ethyl acetate and petroleum ether and was thus obtained as bright yellow prisms melting at 204–205° (Found: C, 63.0; H, 5.0; C<sub>18</sub>H<sub>16</sub>O<sub>7</sub> requires C, 62.9; H, 4.7%). With alcoholic ferric chloride it gave an olive green colour and it dissolved in aqueous alkali freely to give a bright yellow solution slowly changing to brown. It gave an orange-red precipitate with alcoholic neutral lead acetate

and a red colour when an alcoholic solution of it was treated with concentrated hydrochloric acid and magnesium powder. Tambulin has been described as a deep yellow substance melting at 205°. Its colour reactions agree with those given above.

*3:5-Diacetoxy-7:8:4'-trimethoxy flavone*

The above compound (II) (0.1 g.) was treated with acetic anhydride (5 c.c.) and a few drops of pyridine. The solution was kept gently boiling for two hours and poured into water. When all the acetic anhydride had been decomposed, a colourless solid separated out. It was filtered and crystallised from ethyl acetate, when it came out as colourless rectangular rods and flat needles melting at 164–65°; tambulin acetate was recorded to melt at 160–61° (Found: C, 62.0; H, 5.0; C<sub>22</sub>H<sub>20</sub>O<sub>9</sub> requires C, 61.7, H, 4.7%). It did not give any colour with alcoholic ferric chloride and was insoluble in aqueous alkali.

SUMMARY

Based on the evidences recorded in the past the constitution of tambulin is considered to be 7:8:4'-O-trimethyl-herbacetin. A substance of this constitution is synthesised by the partial demethylation of herbacetin-pentamethyl ether and is found to agree very closely with tambulin in properties. Hence its constitution is considered to have now been established.

REFERENCES

1. Bose and Bose .. *J. I. C. S.*, 1939, 16, 183.
2. Balakrishna and Seshadri .. *Proc. Ind., Acad. Sci. A*, 1947, 26, 72.
3. Neelakantam, Rao and Seshadri .. *Ibid.*, 1943, 17, 26.
4. Rao and Seshadri .. *Ibid.*, 1945, 22, 383; *J. C. S.*, 1946, 771; 1947, 122.
5. Goldsworthy and Robinson .. *J. C. S.*, 1938, 56.