

A NOTE ON THE CONSTITUTION OF ALPINETIN

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FROM the ether extract of the seeds of *Alpinea chinesis*, Kimura¹ isolated alpinetin having a melting point of 223°. Based on a study of its properties and reactions, he considered it to be 5-hydroxy-7-methoxy-flavanone. A substance of this constitution had already been prepared synthetically by Shinoda and Sato² and its melting point recorded as 101°. They made it by the partial methylation of 5:7-dihydroxy-flavanone using diazomethane. In view of this discrepancy, 5-hydroxy-7-methoxy flavanone has now been prepared in a different way by the partial demethylation of 5:7-dimethoxy flavanone using aluminium chloride in nitrobenzene solution. In its properties it agrees with the description of Shinoda and Sato and it melts at 101-02°. Alpinetin cannot, therefore, be identical with this flavanone and its constitution should be considered as unsettled.

EXPERIMENTAL

5:7-Dimethoxy-flavanone.—

4:6-Dimethoxy-2-hydroxy-acetophenone required for the present purpose was prepared by the partial methylation of phloracetophenone as described by Sastri and Seshadri.³ It melted at 88-89° and gave a reddish brown colour with ferric chloride.

In the conversion of this ketone into 4:6-dimethoxy-2-hydroxy-chalcone⁴ the yields and the quality of the product could be improved by adopting the following procedure.

A mixture of 4:6 dimethoxy-2-hydroxy-acetophenone (3 g.) and benzaldehyde (9 c.c.) was dissolved in alcohol (20 c.c.) and treated with a strong solution of potash (25 g. of potash in 20 c.c. of water) while cooling in ice. Enough alcohol was then added to get a homogeneous solution and the flask tightly stoppered and left for 3 days at the room temperature. The contents were then diluted with water, extracted twice with ether (A) and the clear alkaline layer acidified with concentrated hydrochloric acid. The product was extracted with ether and the ether solution washed well with aqueous sodium bicarbonate. On distilling off the ether the chalcone was obtained as a red liquid which soon solidified. Yield, 4.0 g.; m.p. 90-91°.

When the ether extract (A) was evaporated, it left a reddish brown oily residue. It was treated with excess of petroleum ether and the mixture kept in the ice-chest. A pale yellow crystalline solid separated out. It was filtered, washed with small quantities of ether and crystallised from a mixture

of benzene and petroleum ether from which it separated in the form of colourless rectangular plates and prisms melting at 143–44°. It was identical with the flavanone described below (Kostanecki and Tambor recorded the melting point of 5:7-dimethoxy flavanone as 1.

For the conversion of the chalkone into the flavanone the former was refluxed with aqueous alcoholic sulphuric acid for 24 hours. The product was ground well with aqueous alkali to remove unchanged chalkone, washed with a little ether to remove coloured impurities and finally crystallised from benzene-petroleum ether mixture. The flavanone separated out as colourless rectangular plates and prisms melting at 143–44°. It was insoluble in aqueous alkali and did not give any colour with ferric chloride. In concentrated nitric acid it dissolved to produce an intense blue colour. When reduced with magnesium and hydrochloric acid in an alcoholic solution, it gave an orange yellow colour.

5-Hydroxy-7-methoxy-flavanone.—

A solution of 5:7-dimethoxy-flavanone (0.5 g.) in dry nitrobenzene was treated with a solution of anhydrous aluminium chloride (1 g.) in the same solvent. After keeping the solution at 100° for 1 hour, it was cooled and treated with excess of petroleum ether, whereby most of the nitrobenzene was dissolved, leaving behind a greenish semi-solid mass. It was washed twice with petroleum ether and finally decomposed with dilute hydrochloric acid. The solution along with the solid product was extracted with ether and the ether solution repeatedly shaken with dilute sodium hydroxide solution. A bulky precipitate separated at this stage in the aqueous medium but this dissolved on adding more of water. The alkaline solution was filtered and acidified with hydrochloric acid. The precipitated solid was filtered, washed with water and crystallised successively from alcohol and a mixture of benzene and petroleum ether. 5-Hydroxy-7-methoxy-flavanone crystallised in the form of stout prismatic needles melting at 101–02°. (Found: C, 71.1; H, 5.4; CH₃O, 11.0; C₁₆H₁₄O₄ requires C, 71.1; H, 5.2 and CH₃O, 11.5%.)

It was sparingly soluble in cold aqueous alkali. In alcoholic solution it gave a deep brown colouration with ferric chloride and an orange colour with magnesium and hydrochloric acid. In concentrated nitric acid it dissolved to a fine blue solution.

REFERENCES

1. Kimura ... *Chemical Abstracts*, 1940, 4063.
2. Shinoda and Sato ... *Ibid.*, 1929, 837.
3. Sastri and Seshadri ... *Proc. Ind. Acad. Sci., A*, 1946, 23 (see next issue of the *Proceedings*).
4. Kostanecki and Tambor ... *Ber.*, 1899, 2260.