OCCURRENCE OF FREE BUTEIN AND BUTIN IN THE FLOWERS OF *BUTEA FRONDOSA*

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FLAVANONES and chalkones are closely related groups of compounds and are easily interconvertable. For a long time it was thought that in nature chalkones occur exclusively. During the past twenty years methods have been developed for distinguishing readily and definitely between the two classes of compounds. As a result of this, most of the naturally occurring glycosides such as hesperidin, naringin, etc., came to be realised as flavanone derivatives. Chalkones seem to be occurring in nature comparatively infrequently. Carthamine and isocarthamine are claimed to be chalkone glycosides but the evidence does not seem to be quite conclusive. Hence whether butein, one of the fundamental chalkones, occurs free as such in plant products or is obtained only as a result of chemical transformation is a question of great interest.

Hummel and Perkin[1] recorded the isolation of a small quantity of butein from the flowers of *Butea frondosa* and mentioned that it occurs free only in small traces, the major component of the petals being a glucoside of butin. They boiled an aqueous extract of the flowers with sulphuric acid and obtained butin as the main product and butein as the minor product (0·04%). Even this quantity of butein was suspected to be the result of chemical transformation of butin. Lal and Dutt[2] who were the first to isolate butrin, a diglucoside of butin, by careful extraction avoiding acid treatment obtained as a byproduct 0·003% of butein. They treated the alcoholic extract of the flowers with neutral and basic lead acetate solutions in succession, and by the decomposition of the neutral lead salt with hydrogen sulphide isolated butein. In a recent paper Price[3] has studied the yellow pigment present in the Dahlia. He has obtained obviously a very small quantity of butein and seems to be under the impression that his is the first recorded instance of the occurrence of this pigment free in nature. The method adopted by him involves treatment with boiling 0·5% hydrochloric acid for 2 hours and this may not be altogether an indifferent process. In all these cases free butin was not detected.

It has now been found that by using the method of extraction described in the experimental part that butein exists in the free condition in the flower petals of *Butea frondosa* to the extent of about 0·3% and that butin accompanies it in small quantities (0·04%). The treatment employed is so mild that there can be no chemical change which could account for their being formed as secondary products. The important features of the method are (1) the extraction of the aglucones with ether from an aqueous solution of the pigments, (2) their ready solubility in aqueous sodium bicarbonate by means of which they can be extracted from the ether solution and purified and (3) the separation of butin from butein in virtue of the greater solubility of the former in water.

Experimental

3 Kilo-grams of the dried flower powder were extracted repeatedly with petroleum ether or carbon tetrachloride in a large continuous extractor on Soxhlet model in batches of 600 g. for about 30–40 hours. This preliminary treatment removed completely waxy material without extracting any of the yellow colouring matter. Subsequently the powder was rendered free from the last traces of the solvent by blowing air through it and then repeatedly extracted for about 30 hours with 95% alcohol until further extraction gave an almost colourless solution. The alcoholic solution was distilled under reduced pressure to remove the solvent as completely as possible. The residue was treated with a large excess of boiling water (about 2 litres) and allowed to cool. It was found that a clear solution was produced and no resinous solid matter separated out. The solution which was deep orange-yellow in colour was then repeatedly extracted with small quantities of ether till no more colouring matter was extracted and the ether layer was colourless. The collected ether extract was shaken in the cold repeatedly with 1% aqueous sodium bicarbonate. The alkaline aqueous layer rapidly turned red and it could be easily separated from the greenish ether layer. The extraction was continued until the bicarbonate extracted no more colouring matter and remained colourless. A subsequent extraction with aqueous sodium carbonate removed very little colour and hence this extraction was omitted.

The bicarbonate extracts were rendered quickly acid by means of dilute hydrochloric acid so that there might be no possible decompositions. The acid solutions were combined and repeatedly extracted with fresh ether. All the colouring matter was thus extracted and when the ether solution was distilled, it was left behind in a fairly clean condition. It was then dissolved in about 100 c.c. of 95% alcohol and the solution set aside for a week when an orange yellow crystalline solid slowly separated out. This was

recrystallised from dilute alcohol when it was obtained in the form of golden yellow stout needles or rods melting with decomposition at 213–15°. (Found: C, 61·9; H, 4·7; loss on drying at 140°, 6·5%. $C_{15}H_{12}O_5$, H_2O requires C, 62·1; H, 4·8; and loss of H_2O 6·2%.) An alcoholic solution of the substance gave with ferric chloride an olive brown colour and with neutral lead acetate an orange red precipitate. With magnesium and hydrochloric acid it gave rise to no anthocyanin colour indicating the absence of flavanones. The substance was thus identified as butein.

The alcoholic mother liquor from which butein had separated was allowed to concentrate by spontaneous evaporation for one week when a further crop of yellow crystalline solid was obtained. Even after crystallisation from alcohol it melted indefinitely at about 208° and was only pale yellow in colour. It seemed to be a mixture of butein and butin. After all the colouring matter was removed, the alcoholic mother liquor finally contained some slimy resin. The separation of butein and butin was effected by boiling the mixture with about 20 c.c. of water and filtering. The residue on the filter was orange yellow in colour and when crystallised from alcohol was found to be pure butein. The aqueous filtrate slowly deposited a pure yellow crystalline solid (broad rectangular plates). After repeated recrystallisation from small quantities of water it exhibited prominent sintering at about 112° (dehydration) and melted at 224–26°. (Found: C, 59·0; H, 5·4 and loss on drying 12·0%. $C_{15}H_{12}O_5$, $2H_2O$ requires C, 58·4; H, 5·2; and loss of H_2O 11·7%.) The anhydrous sample was much lighter in colour. An alcoholic solution gave with ferric chloride a deep green colour and with neutral lead acetate only a dull yellow opalescence. By the addition of a little magnesium powder to the alcohol solution, followed by a few drops of concentrated hydrochloric acid, a brilliant violet colour was developed. This is characteristic of flavanones. From all these properties and reactions it was identified as butin. It may be mentioned here that the dihydrate loses all its water at 100° and there is no further loss on using a higher temperature.

During the course of our experiments it was realised that the mixture of butein and butin could be obtained readily from the ether extract mentioned above by another method. The solution was distilled to remove three-fourths of the solvent and a large excess of petroleum ether added. An orange yellow semi-solid mass readily separated out and turned crystalline on being scratched with a glass rod. Further separation of this mixture was effected as already described.

By the methods adopted above the isolation of the aglucones was quite complete. The ether solution, after the aqueous carbonate extractions,

contained only traces of waxy and amorphous resinous matter. The mixture of free butein and butin was found to be 0·34% on the weight of the air-dry flowers, of which 0·3% was butein and the rest butin.

Summary

A new method of isolating butein and butin from the flowers of *Butea frondosa* is described. The total yield of the aglucones is 0·34% on the weight of the air-dry flowers. By separating them using boiling water, it has been found that butein exists to the extent of 0·3% and butin 0·04%.

REFERENCES

1. Hummel and Perkin .. *J.C.S.*, 1904, 1463.
2. Lal and Dutt .. *J.I.C.S.*, 1935, 262.
3. Price . *J.C.S.*, 1939, 1017.