THE GLYCOSIDIC COMPONENTS OF THE FLOWERS OF *BUTEA FRONDOSA*

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Received March 24, 1941

The flowers of *Butea frondosa* find use in fairly large quantities even at the present time. In the course of a detailed study of the chemical composition it has been found necessary to separate the different types of components carefully. By an initial extraction with petrol the flower wax was isolated and its chemical composition was described.[1] The de-fatted material was extracted with alcohol and by subsequent treatment of the concentrated extract with water and ether, butin and butein were isolated.[2] Continuing the work it has now been possible to obtain butrin in a high state of purity and in high yield without the difficulty that is experienced when employing the method of the previous workers.[3] This is obviously due to the removal of interfering impurities in the earlier stages.

Hydrolysis of this glucoside with dilute sulphuric acid has been stated to yield the flavanone, butin. Similar statements have been made regarding other flavanone glycosides such as naringin, hesperidin, etc. Carefully purified butrin has now been hydrolysed with dilute sulphuric acid and the product examined using the method that has been already described for the separation of the two isomeric compounds, the flavanone and the chalkone. As the result it is noticed that along with butin which is the major part some quantity of butein is also produced. Since particular care has been taken to employ a pure sample of butrin which is free from chalkone derivatives, the formation of butein during the hydrolysis is definite. This conclusion is further supported by other (unpublished) results relating to this group of compounds. It therefore becomes necessary to look for two isomeric products whenever flavanone glycosides are subjected to hydrolysis with acids.

Further in the course of this work two colourless crystalline compounds have also been isolated one of which is a phytosterolin and the other an unidentified heteroside. They were obtained in very small amounts. The former yields on hydrolysis a phytosterol, $C_{28}H_{40}O$ and glucose. The heteroside has the formula $C_{23}H_{40}O_{10}$ and yields on hydrolysis glucose and an aglucone melting at 220°. Both the heteroside and its aglucone do not give

the usual colour reactions of flavanones or chalkones. Further work on these glucosides is in progress.

Experimental

The dry flower powder was extracted first with petroleum ether and subsequently with alcohol as already described.[2] The concentrate of the alcoholic extract was poured into a large excess of water and the orange yellow solution was repeatedly extracted with small quantities of ether to remove the aglucones. The extracts were separated (A) and preserved for examination. The aqueous solution (2 litres from 3 kg. of the flowers) was allowed to stand saturated with ether. In the course of a few days a pale yellow solid separated out in the form of thin flakes (B). It did not give any of the colour reactions of flavanones or chalkones and it is described later in this paper. After the separation of the above solid the solution was again allowed to stand with the addition of some more ether in order to keep it saturated. In the course of a week about 1·5% yield of butrin separated out in a crystalline condition. More was obtained on longer standing and on concentrating the solution at the ordinary temperature and subsequently saturating it with ether. The solid was pale yellow in colour and contained a small amount of mineral matter. It was further purified by one re-crystallisation from hot rectified spirits when it was obtained as colourless long needles melting at 194–95° (decomp.). When crystallised from water however, the crystals take the form of aggregates of micacious plates. Though the yield of crude butrin obtained by the method of Lal and Dutt is considerably high (about 2·5%), after passing through the several stages of purification the yield of the pure product becomes less than 0·4%. The glycoside is fairly soluble in water and when impure its solubility is markedly high. The highly soluble impure sample has been said to contain metallic salts of the pigment.[3] But there seems to be no definite support for this view and all data point towards the colloidal condition of the substances as the cause of solubility (compare Seshadri[4]). The presence of a little mineral matter is nothing unusual in crude substances isolated from plant materials.

Butrin (1·2 g.) was treated with 7% aqueous sulphuric acid (50 c.c.) and the mixture boiled for about 2 hours. The clear solution deposited on cooling a brown precipitate in a crystalline condition. After filtering and washing with water it gave reactions for butin, a green colour with alcoholic ferric chloride and violet colour with magnesium and alcoholic hydrochloric acid. Close examination of the solid indicated that it was a mixture. A small quantity of more highly coloured crystals could be picked out and these gave tests for butein. Complete separation was however effected using boiling water (20 c.c.) and filtering hot. The less soluble portion on the filter was

repeatedly washed with small quantities of hot water and finally crystallised from dilute alcohol. It was found to be identical with butein in all respects. It gave an olive brown colour with alcoholic ferric chloride, an orange red solution with alkali and it did not respond to the anthocyanin test using magnesium and alcoholic hydrochloric acid. It melted at 215° and the melting point was not depressed by admixture with an authentic sample of butein. The yield of this chalkone amounted to 6% of the aglucone mixture. From the aqueous filtrate pale yellow crystals of butin dihydrate were isolated. Longer heating during the course of hydrolysis did not produce any difference in the yield of the two isomeric aglucones nor did the substitution of 7% hydrochloric acid for sulphuric acid for purposes of hydrolysis make any change in the result. An estimation of the products of hydrolysis (aglucone mixture and glucose) was made with a view to confirm the composition of butrin as diglucoside. The aglucones were extracted repeatedly with ether and weighed after evaporating the solvent and air-drying. For purposes of calculation the product was taken to be butin dihydrate. The sugar was estimated by titration with Fehlings solution. (Found: aglucone 45·0, glucose 55·3; $C_{27}H_{32}O_{15}$, $2H_2O$ requires aglucone 48·7 and glucose 57·0%.)

Isolation of a phytosterolin. The ether extract (A) was shaken with aqueous sodium bicarbonate with a view to extract the butin-butein mixture from it. During this operation a colourless solid separated out being insoluble in both the aqueous and ether layers. It was ordinarily found suspended at the bottom of the ether layer. It was filtered and washed with more ether. It was sparingly soluble in ether, chloroform, ethyl acetate and even in alcohol. But it was easily soluble in glacial acetic acid and in pyridine. It was therefore purified by successive treatment with boiling ether and alcohol to remove impurities and by a final crystallisation from dilute pyridine. The pure substance appeared as colourless hexagonal plates and melted at 260–62° (decomp.). It yields a blood red colour with chloroform and sulphuric acid (Hesse's reagent) and a display of colours, pink – blue – green with the Liebermann Burchard reagent. Thus it gives the typical sterol reactions. (Found in the sample dried at 120° for 2 hours: C, 71·7; H, 11·5; $C_{34}H_{62}O_6$ requires C, 72·1; H, 11·0%.) The substance was hydrolysed with amyl alcoholic hydrochloric acid and the amyl alcohol was removed by steam distillation. By ether extracting the residual aqueous mixture was obtained sitosterol melting at 145–46°. The aqueous solution was found to contain glucose. The yield of the phytosterolin was very small being about 0·02% of the flowers taken.

Heteroside (*B*).—The pale yellow solid, as it was first obtained, melted at about 212°. It was purified by dissolving in excess of alcohol and allowing to cool slowly when it separated out as a colourless crystalline solid. This

was filtered and repeatedly washed with small quantities of warm water. In order to get more of the substance the alcoholic mother liquor was concentrated to small bulk, treated with water till it became just turbid and the mixture allowed to stand. Shining colourless crystals were thereby obtained and the final aqueous mother liquor contained a small quantity of butrin. The purified heteroside was insoluble in water, ether and chloroform, and moderately easily soluble in hot alcohol. It was however readily soluble in glacial acetic acid and pyridine and it was obtained in the form of colourless hexagonal plates by crystallising from a mixture of water and pyridine. It melted at 236–37° with decomposition. It was insoluble in aqueous sodium carbonate or hydroxide and gave no colour with alcoholic ferric chloride or with magnesium and alcoholic hydrochloric acid. The last reaction could be employed as a sensitive test for the existence of butrin as an impurity since even a small quantity of it gives a noticeable pink colour. The heteroside dissolved in concentrated sulphuric acid to produce a bright orange red solution the colour of which deepened on standing and changed to deep purple in the course of about 12 hours. With chloroform and concentrated sulphuric acid (Hesse's reagent) it formed a pale yellow solution whereas with chloroform, acetic anhydride and a drop of concentrated sulphuric acid (Liebermann-Burchard reagent) a pink solution was produced which slowly changed to brown on standing. These reactions indicate that the substance does not belong to the group of sterols but may be related to the resinols. (Found in the sample dried at 120°: C, 57·4; H, 8·6; $C_{23}H_{40}O_{10}$ requires C, 57·9; H, 8·4%.) When hydrolysed with amyl alcoholic hydrochloric acid it yielded glucose and a colourless aglucone melting at 220° C. The aglucone gave reactions very similar to those of the heteroside but dissolved easily in alcohol, chloroform and ether. Further work on this substance is in progress.

Our thanks are due to Mr. G. V. L. Narasimha Murty for some of the micro-analyses.

Summary

Butrin has been obtained by a simple method and in good yield from the flowers of *Butea frondosa*. On hydrolysis with acids it gives a mixture of butin and butein. Two colourless crystalline compounds have also been isolated, one of which is a phytosterolin and the other an unidentified heteroside.

REFERENCES

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