CXLVII.—*The Colouring Principle of the Flowers of the Butea Frondosa.*

By ARTHUR GEORGE PERKIN, F.R.S., and, in part, the late JOHN JAMES HUMMEL.

THE *Butea frondosa*, also called *Dhak* or *Pulas*, is a fine tree, thirty to forty feet high, belonging to the order *Leguminosæ*; it is common throughout India and Burma, and is found in the North-West Himalaya as far as the Jhelum River. The flowers, which, in the

dried condition, are known as *tísú, késú, kesuda,* or *palás-képpúl,* have a bright orange colour, and, although they are much larger, closely resemble in appearance the common gorse flower (*Ulex europœus*), with which, indeed, they are botanically allied. An almost unlimited supply of these flowers can be obtained, and large quantities are collected in March and April, dried in the sun, and employed by the natives to produce a yellow dye, much used during the Holi festival. The dyeing operation, which consists of steeping the material in a hot or cold decoction of the flowers, is virtually a process of staining, because the colour can be readily washed out, and this is, indeed, considered an advantage and is frequently effected at the end of the festival. On the other hand, a more permanent result is sometimes produced either by first preparing the cloth with alum and wood-ash or by adding these substances to the dye-bath. Occasionally other dyes are employed along with the flowers, such as annatto, turmeric, or myrabolans, either with the object of modifying the colour obtained or to render it less fleeting. From the *Butea frondosa* is also obtained the so-called " Butea gum " or " Bengal kino " employed by the natives for tanning leather, and the tree is of additional interest because in many parts of India the lac insect (*Coccus lacca*) is reared on it. This, as is well known, causes the formation of stick lac, from which shellac and lac dye are prepared.

A preliminary examination of these flowers was made some years ago by Hummel and Cavallo (Proc., 1894, 10, 11), who isolated a substance which they termed butein, to which they assigned the formula $C_{15}H_{14}O_5$, supposing this substance to be the true colouring matter. This product, which was present in the plant in the form of glucoside, in some respects yielded shades which were not unlike those of the fisetin obtained from young fustic. More recently, Hill (Proc., 1903, 19, 133), who, although aware that the subject had been previously studied, had not access to the original papers, extracted from these flowers a colouring matter in the form of small, lemon-yellow crystals which gave the reactions of fisetin. He noted further the presence of a tannin matter which readily yields a phlobophane, and found that the latter, on fusion with potassium hydroxide, gave phloroglucinol and protocatechuic acid.

For a liberal supply of the raw material, we are indebted to the authorities of the Imperial Institute.

EXPERIMENTAL.

The most rapid method for the isolation of the colouring principle is that originally employed by Hummel and Cavallo (*loc. cit.*), and consists in digesting an aqueous decoction of the flowers at the boiling

point with a little sulphuric acid to hydrolyse the glucoside, and extracting the product with ether. For this process, very large quantities of ether were necessary, and the following more economical method was therefore devised.

One thousand grams of the flowers were digested for six hours with boiling water, and the extract treated with 50 c.c. of sulphuric acid and again heated for one hour. A light, viscous precipitate, devoid of dyeing property, had then separated, and this was removed while hot, and the filtrate left overnight. The clear liquid was now decanted from a small quantity of tarry substance (A), which was reserved for further examination, and gently evaporated for three hours on the water-bath. A further quantity of a black, viscous product was thus deposited, and when this had been removed the filtrate, after some days, deposited crystals, the yield of which was usually from 18 to 20 grams or approximately 2 per cent., but varying according to the prevailing temperature. Again, if the evaporation was carried too far, a destruction of the colouring principle appeared to ensue and the quantity isolated was small. For purification, the product was dissolved in a little alcohol, the mixture poured into ether, and the solution repeatedly agitated with water until the washings were no longer of a dark colour. The ethereal liquid was evaporated, the residue dissolved in hot alcohol, the solution treated with a very little boiling water, and the substance which separated on cooling recrystallised in a similar manner until pure. After drying at 160°, an analysis gave the following result :

Found, $C = 66 \cdot 00$; $H = 4 \cdot 56$.
$\qquad$ $C_{15}H_{12}O_5$ requires $C = 66 \cdot 17$; $H = 4 \cdot 41$ per cent.

For this substance, the name *butin* is now proposed in preference to the term butein originally assigned to it, because, as will be seen later on, it is not the true colouring matter, but rather the colouring principle from which the dye is derived.

When thus obtained, butin crystallises in small, colourless needles melting at 224—226°, but if much water be employed for its separation the crystals then have a pale yellow tint. The air-dried product usually contains $\frac{1}{2}H_2O$, which is evolved at 160°.

Found, $H_2O = 3 \cdot 23$. $C_{15}H_{12}O_5, \frac{1}{2}H_2O$ requires $3 \cdot 20$ per cent.

But, on the other hand, if butin is crystallised from boiling water, in which it is sparingly soluble, it is deposited in pale yellow leaflets having the formula $C_{15}H_{12}O_5, 2H_2O$.

Found, $H_2O = 11 \cdot 33$; $11 \cdot 79$. $C_{15}H_{12}O_5, 2H_2O$ requires $11 \cdot 68$ per cent.

It sometimes happens, however, that both these forms are produced

from the same solution, in which case the compound $C_{30}H_{24}O_{10},H_2O$ is first deposited.

Butin is readily soluble in alcohol, somewhat more sparingly so in acetic acid or ether, and almost insoluble in benzene.   With alcoholic lead acetate it gives a pale yellow, almost colourless precipitate, and with alcoholic ferric chloride a deep green liquid is produced.   When treated with cold sulphuric acid, it does not at first dissolve, but assumes a deep red colour as if an acid compound was produced ; this subsequently passes into solution with the formation of a pale yellow liquid.   With acetic and sulphuric acids, however, no crystalline acid compound separates, and alcoholic potassium acetate does not cause the deposition of a mono-potassium salt.   Butin does not contain methoxy-groups.

Acetylbutin may be prepared in the usual manner by means of acetic anhydride and sodium acetate, but as viscous by-products are simultaneously produced, a modification of Deninger's benzoylation process was chiefly employed.   Two grams of butin dissolved in 30 grams of pyridine were mixed with 10 grams of acetyl chloride, and after one hour the mixture was poured into water, the insoluble residue washed several times by decantation, and dissolved in a mixture of acetone and alcohol.   Crystals gradually separated which were purified by recrystallisation from the same solvents.

Found, $C = 63·35$; $H = 4·87$.
$C_{15}H_9O_5(C_2H_3O)_3$ requires $C = 63·32$; $H = 4·52$ per cent.

A molecular weight determination by the cryoscopic method gave the following result :

0·2390 in 13·15 naphthalene gave $\Delta t - 0·31°$; M. W. $= 410$.
$C_{21}H_{18}O_8$ requires M. W. $= 398$.

The acetyl determination was carried out by the method previously described (Proc., 1904, **37**, 171), employing (*a*) alcoholic sulphuric acid, and (*b*) alcoholic potassium acetate.

Found, acetic acid (*a*) $= 45·34$, 45·60, and (*b*) $= 45·60$.
$C_{15}H_9O_5(C_2H_3O)_3$ requires $C_2H_4O_2 = 45·22$ per cent.

Acetylbutin crystallises in colourless leaflets melting at $123—125°$, readily soluble in hot alcohol.

Benzoylbutin, which is readily prepared by Deninger's method, employing 2 grams of butin, 30 grams of pyridine, and 23 grams of benzoyl chloride, was isolated in the usual manner and crystallised from a mixture of benzene and alcohol.

Found, $C = 74\cdot02$; $H = 4\cdot05$.

$C_{15}H_9O_5(C_7H_5O)_3$ requires $C = 73\cdot97$; $H = 4\ 10$ per cent.

$0\cdot3615$ in $13\cdot99$ naphthalene gave $\Delta t - 0\cdot31^\circ$; M. W. $= 583$.

$C_{36}H_{24}O_8$ requires M. W. $= 584$.

Tribenzoylbutin forms colourless needles melting at $155—157^\circ$, sparingly soluble in alcohol. These results therefore indicate that butin has the formula $C_{15}H_{12}O_5$ and contains three hydroxyl groups.

On fusion with caustic potash and a little water at $200—220^\circ$ butin gives protocatechuic acid (m. p. $194—196^\circ$) and resorcinol (m. p. $107—109^\circ$).

The Conversion of Butin into the Colouring Matter Butein.

Butin dissolves readily in cold alkaline solutions, forming a pale, orange-red liquid, which, when at once acidified, deposits the unchanged substance. On boiling the solution in potassium hydroxide, however, the colour rapidly darkens, and if acid is now added a bright orange, crystalline precipitate almost immediately separates, which is rapidly collected and washed with boiling water. The filtrate, on cooling, deposits unattacked butin, but if this is again made alkaline and heated to boiling a further quantity of the new substance may be thus obtained. The product was further purified by crystallisation from dilute alcohol and dried at 160°.

Found, $C = 66\cdot26$; $H = 4\cdot66$.

$C_{15}H_{12}O_5$ requires $C = 66\cdot17$; $H = 4\cdot41$ per cent.

This substance, to which the name *butein* is assigned, forms glistening, reddish-orange needles melting at $213—215^\circ$; when deposited from dilute alcohol, it contains water of crystallisation which can be removed at 100°.

Found, $H_2O = 6\cdot26$. $C_{15}H_{12}O_5,H_2O$ requires $H_2O = 6\cdot21$ per cent.

If butin is digested with boiling alcoholic potassium acetate for some time, butein is produced in small quantity, and this change appears also to occur slowly when a boiling alcoholic solution of butin is treated with a little dilute sulphuric acid. Boiling alcoholic potash also behaves in a similar manner, but somewhat less energetically than the aqueous alkali.

Butein is readily soluble in alcohol and to some extent in ether, but is much more sparingly soluble than butin in hot water, a fact which is of assistance in separating these two substances ; it dissolves in alkaline solutions to a deep orange-red solution, and with a similar tint in boiling alcoholic potassium acetate, but no insoluble monopotassium salt is thus formed. Alcoholic lead acetate gives a deep red precipitate, and alcoholic ferric chloride an olive-brown coloration. In

cold sulphuric acid it is sparingly soluble forming an orange solution, and the suspended substance assumes the same colour; this indicates the formation of an acid compound, for on dilution with water the colour is discharged and the butein reprecipitated in an unchanged condition. It is energetically attacked by nitric acid (sp. gr. 1·42), a deep brown liquid being thus produced.

Acetylbutein is best prepared by the pyridine method, employing the same proportions as were serviceable in the case of acetylbutin. The product crystallised from alcohol in extremely pale yellow or almost colourless needles melting at $129-131°$.

Found, $C = 62·54$; $H = 4·79$.

$C_{15}H_8O_5(C_2H_3O)_4$ requires $C = 62·72$; $H = 4·55$ per cent.
$0·4287$ in $13·64$ naphthalene gave $\Delta t - 0·47°$.   M. W. $= 467$.

$C_{23}H_{20}O_9$ requires M. W. $= 440$.

The acetyl groups were determined by Liebermann's method, for this was possible on account of the sparing solubility of butein in water. The acetic acid was also estimated by the method employed with acetylbutin.

Found, butein $= 61·61$; acetic acid $= 54$.

$C_{15}H_8O_5(C_2H_3O)_4$ requires $C_{15}H_{12}O_5 = 61·81$; $4C_2H_4O_2 = 54·54$ per cent.

It is therefore evident that butein has the same formula as butin, but, on the other hand, whereas butin contains three hydroxyls, in butein four such groups are present.

An attempt to prepare a crystalline benzoylbutein was not successful, the product being of a viscous nature.

The Action of Alkalis on Butein.—When fused with caustic potash at $200-220°$, butein gives the same products as butin, namely, resorcinol and protocatechuic acid. It was of interest to determine whether some more complex product of the hydrolysis could be obtained by a less energetic action of the alkali, as some further insight into the constitution of the substance might be thus obtained.

Two grams of butein dissolved in 50 c.c. of 50 per cent. aqueous caustic potash were boiled until the orange-red colour of the liquid had become brown, and a sample, when neutralised with acid, no longer gave a precipitate of unchanged substance. The solution was now diluted with water, acidified, extracted with ether, and the oily product dissolved in a little dilute caustic potash; this was then saturated with carbon dioxide, again extracted with ether, and the extract evaporated to dryness. The residue was purified by two or three crystallisations from benzene with the aid of animal charcoal.

Found, $C = 62·84$; $H = 5·40$.

$C_8H_8O_3$ requires $C = 63·15$; $H = 5·26$ per cent.

This substance melted at 140—143° and had all the properties of resacetophenone.
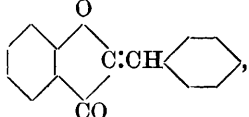
The aqueous liquid from which the resacetophenone had been isolated contained a second substance which was found to consist of protocatechuic acid.

No attempt was made to hydrolyse butin in this manner, for as it was evident that the first action of the alkali would lead to the production of butein, the same final products must result in both cases.

The Dyeing Properties of Butin and Butein.—As butin gives with alcoholic lead acetate an almost colourless precipitate, it cannot be regarded as a colouring matter, whereas the behaviour of butein in this respect (*loc. cit.*) is evidence of its intense tinctorial property. In other words, butin is the colouring principle and butein the colouring matter, and their relationship to one another is therefore somewhat analogous to that which exists between hæmatoxylin and hæmatein, and between brazilin and brazilein. It was interesting to find, however, that butin and butein dyed mordanted woollen cloth in identical shades, and this gave rise, in the earlier stages of this work, to the supposition that butein was merely the quinonoid form of butin. That this is hardly the case will be seen later, but it is nevertheless quite certain that by the action of the mordant butin is converted into butein, and is not to be regarded as a colouring matter itself. The following shades were obtained :

Chromium.	Aluminium.	Tin.	Iron.
Reddish-brown.	Brick-red.	Full yellow.	Brownish-black.

These colours differ somewhat in. character from those given by any known natural colouring matter, although they bear some resemblance to those furnished by quercetin, myricetin, and fisetin, especially as regards the latter compound. On the other hand, these dyeings are strikingly similar to those yielded by some of the

phenylketocumaran colouring matters,

, artificially prepared by Friedlander and Rudt (*Ber.*, 1896, **29**, 879). Although similar in many respects, butein is, however, not identical with the compound :
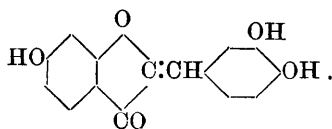
Methylation of Butin.

In the earlier experiments, this operation was carried out in the ordinary way by employing 5 grams of butin, 5 grams of potassium hydroxide in methyl alcohol, and excess of methyl iodide. Subsequently, methyl sulphate was employed, for not only was the action more rapid but a better yield resulted, the products being the same in both cases.

In carrying out the reaction, 10 grams of butin in methyl alcohol were treated with 6·6 grams of potassium hydroxide, and the quantity of methyl sulphate necessary to neutralise the alkali then added. As soon as the reaction had ceased, similar quantities of methyl sulphate and alkali were added for a second and third time. The product was poured into water, the mixture extracted with ether, the ethereal liquid washed with dilute caustic potash solution to remove a trace of partially methylated product, and then evaporated to dryness. A solution of the residue in boiling alcohol slowly deposited crystals, and these, on examination, were found to consist of two substances: (A) sparingly soluble in alcohol, and (B) which is much more readily so. The yield of the mixture was 5 grams.

The substance (A) was purified by frequent crystallisation from alcohol.

Found, $C = 68·88$; $H = 6·07$.

$C_{15}H_9O_2(O·CH_3)_3$ requires $C = 68·79$; $H = 5·73$ per cent.

Thus obtained it formed glistening, yellow leaflets melting at 156—158°, sparingly soluble in the usual solvents. If it is dissolved in hot concentrated alcoholic potash, this solution, on cooling, becomes semi-solid owing to the evaporation of a potassium salt which dissolves on treating the mixture with water, and from which the unchanged ether is redeposited on acidification. The addition of one drop of sulphuric acid to a solution of the substance in acetic anhydride causes the formation of a beautiful magenta-coloured liquid.

The second product (B) separated in needles, which on close examination appeared to be a mixture, for, whereas some were colourless, others had a yellow tint. By repeated fractional crystallisation and by rejecting the first portions this coloured impurity was gradually removed, but its complete separation was exceedingly troublesome. It was not, however, present in large amount, for the frequent purification did not alter the melting point to any marked extent.

Found, $C = 68·54$; $H = 5·95$.

$C_{15}H_9O_2(O·CH_3)_3$ requires $C = 68·79$; $H = 5·73$ per cent.

When thus obtained, it consisted of thin plates melting at $119—121°$, and gave, with acetic anhydride and sulphuric acid, the same magenta coloration as in the case of substance (*A*).

The formation of two trimethyl ethers, having the same composition, by the methylation of butin is, at first sight, somewhat remarkable, but this result is more easily understood on considering the behaviour of butin itself with dilute alkaline solutions, whereby it is converted into butein. This reaction would no doubt occur to some extent during the methylation process, and the two products should consist respectively of the trimethyl ethers of butin and butein. For a variety of reasons, it appeared evident that the colourless substance (*B*) melting at $119—121°$ was the butin derivative, and it was interesting to determine, as a possible confirmation of this point, whether it would be converted by means of alkali into the more sparingly soluble compound (*A*) melting at $156—158°$.

Butin trimethyl ether 1·5 grams were dissolved in 15 c.c. of normal alcoholic potash, and the solution was boiled for a few minutes alone, and subsequently with the addition of an equal volume of water. The product was diluted with water, neutralised with acid, and the precipitate which separated was collected and crystallised from alcohol. It formed yellow leaflets melting at $156—158°$, gave on analysis $C = 68·96$, $H = 5·96$ per cent., and evidently consisted of the butein trimethyl ether (*A*).

When methylated therefore in the foregoing manner, butin yields both butin and butein trimethyl ethers, and the former can be readily converted into the latter by means of potassium hydroxide solution.

Methylation of Butein.

The methylation of butein was now studied by the aid of processes similar to those employed with butin. The results were interesting, for not only was the expected butein trimethyl ether (m. p. $156—158°$) obtained, but it was accompanied in all cases by the butin trimethyl ether (m. p. $119—121°$). It appeared possible at first that the butein employed was contaminated with butin, but this was evidently not the case, for a sample of the colouring matter specially purified on this account gave an identical result. The yield of butin trimethyl ether was greatest when methyl iodide was employed for the methylation, and but little was obtained if strong aqueous potassium hydroxide was added during methylation with methyl sulphate.

Synthesis of Butein Trimethyl Ether.

As butein on hydrolysis gives resacetophenone and protocatechuic acid, it might, if these data alone were considered, be either a flavone or benzylidenecumaran derivative, but its colour reactions, and especially the fact that it contains four hydroxyl groups, render these suppositions untenable.   The only constitution for butein in harmony with its properties appeared to be that of a *tetrahydroxybenzylidene-acetophenone* having the following formula :
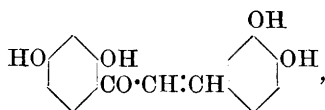
and this has been found correct.   Although Kostanecki and his colleagues have employed numerous compounds of this class in the form of their methyl and ethyl ethers during their extremely interesting syntheses of flavanol derivatives (*loc. cit.*), yet a trimethoxy-hydroxybenzylideneacetophenone which was suspected to be identical with butein trimethyl ether had not been described :
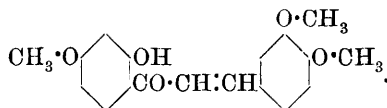
Molecular proportions of resacetophenone methyl ether and veratr-aldehyde were condensed in the presence of alcoholic potash, the product dissolved in water, the solution neutralised with acid, and the yellow precipitate collected and purified by crystallisation from alcohol.

Found, $C = 68.75$; $H = 6.02$.
$C_{15}H_9O_2(O \cdot CH_3)_3$ requires $C = 68.79$; $H = 5.73$ per cent.

It consisted of orange-yellow leaflets melting at 156—158°, and was identical in all respects with the butein trimethyl ether obtained from natural sources.   With acetic anhydride and sulphuric acid, it gave the characteristic magenta coloration.

Butein is accordingly $2 : 4 : 4' : 5'$-*tetrahydroxybenzylideneacetophenone* or $2 : 4 : 4' : 5'$-*tetrahydroxychalkone*.

Synthesis of Butin Trimethyl Ether.

Butin differs from butein in containing only three hydroxyl groups, a fact which was of extreme importance in elucidating its constitution. That in butin the catechol hydroxyls are both intact appeared likely from the fact that it is precipitated by lead acetate as described above,

and consequently it seemed certain that in this substance a hydroxyl
of the resorcinol nucleus was involved in the formation of an anhydride,
thus necessitating the production of a ring. Again, the fact that
butin was not a colouring matter indicated the absence of the ethyl-
enic linkage which occurs in butein. A consideration of these points
and the fact that butin and butein have identical formulæ rendered it
necessary to assume that during the reaction by which the latter is
converted into the former an intermediate stage must first occur. It
therefore seemed probable that butin was a flavanone compound :

$$OH\text{—}\bigcirc\text{—O—CH—}\bigcirc\text{—OH},\quad \text{with } OH \text{ and } CO\text{–}CH_2$$
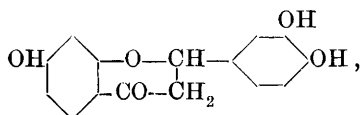
a class of substance recently discovered and synthetically prepared
by Kostanecki and his colleagues (*Ber.*, 1904, **37**, 784, 773, 779), who
have shown that chalkone derivatives, on prolonged digestion with
dilute sulphuric acid, are partly converted into the corresponding
flavanone derivatives, the reaction apparently taking place in the
following manner :

Chalkone.   Intermediate compound.   Flavanone.
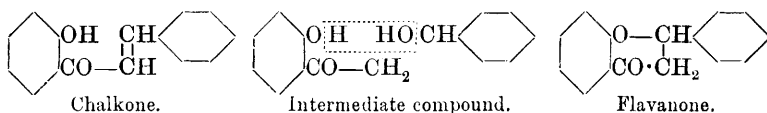
The flavanone methyl ethers have been shown by these authors
to be colourless, which is also the case with the butin methyl ether
under discussion.

In accordance with the method employed by these chemists, artificial
butein trimethyl ether was digested for several hours with 10 per cent.
sulphuric acid, sufficient alcohol being present to bring the substance
into solution. The product, when crystallised from alcohol, deposited
first some quantity of the unattached chalkone, but subsequently a
more soluble compound separated. After numerous crystallisations,
this substance was obtained in an almost colourless condition, and
then melted at 118—120°. It was identical with the butin trimethyl
ether prepared by methylating butin itself, which must therefore be
the 3 : 4′ : 5′-*flavanone*, the formula of which is given above. On diges-
tion with alcoholic potash and a little water, the artificial butin methyl
ether behaved in a similar manner to the natural product, giving
butein methyl ether.

Conversion of Butein into Butin.—Experiments were now carried
out to determine whether butein could be reconverted into butin in a
similar manner. Butein (1·5 grams) dissolved in 50 c.c. of 50 per
cent. alcohol was treated with 2 c.c. of sulphuric acid and the mixture

digested on the water-bath for eight hours. The hot liquid, on cautious dilution with boiling water, gave a precipitate of unaltered butein, which was removed, and the filtrate was treated with more water and left overnight. A quantity of pale yellow needles which had then separated was collected and recrystallised from much boiling water in the presence of animal charcoal. The air-dried product had the formula $C_{15}H_{12}O_5,2H_2O$, melted at $224—226°$, and was evidently identical with butin.

Found, $H_2O = 11.33$.   Found (at $160°$), $C = 66.17$; $H = 4.41$ per cent.

Aqueous potassium hydroxide reconverted the butin thus prepared into butein. The special behaviour of the flavanone butin with alkaline solutions, by which it is converted into the corresponding chalkone, will probably be found to be characteristic of the whole group; as, however, numerous artificial compounds of this class are under investigation by Kostanecki, the subject has not been further studied in this direction.

The ease with which butin is converted into butein and *vice versâ* is very interesting and is worthy of further study from a quantitative standpoint.

This change is readily explained if it is assumed that the intermediate compound (Kostanecki, *loc. cit.*)
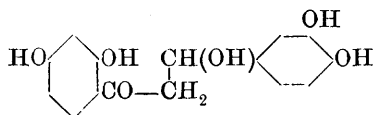
is the first product of the reaction in each case, and that this subsequently, by loss of water, passes into either chalkone or flavanone, or both. It is possible that in no case does the reaction become entirely unidirectional, and it is interesting to notice that a trace of butein has always been found among the products of the hydrolysis of acetylbutin with alcoholic sulphuric acid.

Butein and butin are the first members of the chalkone and flavanone groups which have been isolated from natural sources.

Hill's suggestion (*loc. cit.*) that a colouring matter resembling the fisetin of young fustic is contained in the flowers of the *Butea frondosa* made a search for this substance desirable, and its presence was, indeed, possible because, on account of its sparing solubility in water, it would be deposited with the viscous matter so abundantly produced during the isolation of butin. Should fisetin be present, the constituents of this plant would be of special interest, for it would

then be known to contain the chalkone, the flavanone, and the flavone compounds, illustrating the synthesis carried out by Kostanecki (*Ber.*, 1904, **37**, 784). An alcoholic solution of the tarry product (*A*) was poured into ether, the ethereal liquid well washed and evaporated to dryness. The treacly residue was extracted with boiling water, the extract allowed to cool, and the crystals, which slowly separated, were collected, washed with a little ether, and crystallised from dilute alcohol. The substance formed orange-red needles melting at 213—215°, identical in all respects with butein. By this method, the yield of the colouring matter from a kilogram of the flowers was 0·4 gram, and, although some slight loss would occur during its extraction, the quantity actually present in the plant could not far exceed this amount. It is not certain whether butein or its glucoside exists in the fresh flowers ; such may be the case, although it is quite possible that this colouring matter has been merely derived from the butin during the operations involved in the extraction of the latter. Fisetin does not therefore appear to exist in the flowers of the *Butea frondosa*.

### Action of Sulphuric Acid on Butein.

If a thin paste of butein with acetic acid is treated in the cold with a few drops of sulphuric acid, the mixture becomes orange-red, and, after a few minutes, minute, dull red needles having a steel-blue iridescence separate out. This substance, which is evidently the sulphuric acid compound of butein, is too unstable for isolation, and on washing with acetic acid is reconverted into butein and sulphuric acid.

When butein (0·25 gram) in 5 c.c. of acetic acid is boiled with four drops of sulphuric acid, the orange-red liquid becomes duller in colour and a new substance gradually separates ; this adheres to the sides of the vessel and has a beetle-green iridescence. It is very sparingly soluble in the usual solvents, dissolves in alkaline solutions with a deep blue colour, and under the microscope possesses a distinctly crystalline structure. The acid liquid decanted from this substance on dilution with water deposits a brown precipitate also soluble in alkalis with a bluish-violet coloration, and which dyes mordanted calico with shades of a similar character to those yielded by anthragallol. It appears likely that this more soluble substance represents the first product of the reaction and is subsequently converted into the foregoing dark compound.

A consideration of the formula of butein renders it unlikely that these new substances are anthraquinone derivatives ; on the other hand, it is suspected that the formation of a ring takes place with the

abstraction of water, an indone derivative of the following type being the first product :
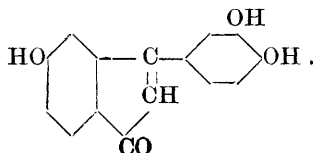
It is likely that other chalkone derivatives will behave in a similar manner, and the subject is reserved for further examination.   Experiments with butin show that in this respect it closely resembles butein, and it is possible that the products thus obtained are identical in both cases.

The Dyeing Properties of the Flowers.

Towards mordanted calico, these flowers are almost inert, evidently because the glucoside of butin which they contain is of too stable a character to be hydrolysed by the mordant.   In wool dyeing where acid baths are employed, a better result is obtained, although in this case the shades possess but little strength.   If the glucoside is first hydrolysed by boiling the flowers with dilute hydrochloric acid and the mixture evaporated to dryness, or if sulphuric acid is employed, and the acid then neutralised with sodium carbonate, a material is obtained which dyes readily by the usual methods.   Such products gave the following shades : with chromium, deep terra-cotta ; with aluminium, a bright orange ; with tin, bright yellow ; and with iron, a brownish-olive.   The chromium colour is characteristic and is much redder in tint than that yielded in this way by any known natural yellow dye. These colours are somewhat fugitive to light, and the *Butea frondosa* flowers cannot therefore be classed among the more valuable natural yellow colouring matters.

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