

## A NOTE ON THE PHLOBATANNINS OF KINO AND BUTEA GUMS

BY G. V. KRISHNAMURTI AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University)

Received July 16, 1945

DUE to the serious dearth of synthetic dye-stuffs during the past several years as a result of war, attention has been directed in India to the revival of plant dyes. There has been a number of cases, where materials, which contain predominantly phlobatannins, have been successfully used for dyeing. Among these the Kino and Butea gums seem to be the most important. The first is obtained from the trees of *Pterocarpus marsupium* and is also known as Malabar kino. The second is less frequently used and is obtained from the trees of *Butea frondosa*. Both plants belong to the same natural order, Leguminosæ. The above two gums have now been examined with a view to compare the phlobatannins present in them and also to obtain more information about this group of complex compounds.

Gum kino has been examined by several workers in the past, the most important contribution to our knowledge being that of Simonsen<sup>1</sup> in whose paper all previous work is conveniently summed up. He methylated and acetylated the kino directly. The kino methyl ether was obtained in the form of an almost colourless amorphous powder which did not melt below 300° and the acetyl compound was a brown amorphous powder. Analyses of these suggested the formula  $C_{15}H_{11}O_4(OH)_3$  for the kino. It was considered to form a trimethyl ether and a triacetyl derivative. The molecular weight indicated that the molecule is at least twice that suggested by this formula. Fusion of the kino with potassium hydroxide yielded protocatechuic acid and oxidation of the kino methyl ether with alkaline potassium permanganate gave veratric acid. These proved the presence of a catechol unit.

In view of the suggestion that phlobatannins have a 4-hydroxy-flavpinacol structure<sup>2</sup> it seemed to be desirable to obtain pure and colourless derivatives of these substances and see if they exhibit optical activity. The work done with this object in view is described in this note.

Kino and Butea gums have now been subjected to purification with a view to eliminate gummy matter and ether-soluble impurities. The purified

phlobatannins have been methylated and acetylated following in general the procedure of Simonsen. The methyl ethers and acetates are thereby obtained in an almost colourless condition. The former are amorphous powders ; the latter appear to be crystalline though the crystalline appearance is not definite. These substances exhibit marked optical activity thus providing support for the hydroxy-flavan structure for phlobatannins. The methyl ethers are quite stable to the action of aqueous hydrochloric acid whereas the parent phlobatannins quickly change under these conditions into insoluble phlobaphenes. This seems to indicate that the conversion requires the presence of free phenolic groups.

From the reactions and analytical results presented towards the end of the paper it appears that the phlobatannins of kino and Butea gums are identical. This is also supported by experiments on dyeing in which very similar results are obtained using the two gums.

#### EXPERIMENTAL

*Purification of Kino gum.*—Kino gum (10 g.) was dissolved in boiling water (100 c.c.) and the solution filtered. The clear cold filtrate was treated with saturated brine and the precipitated tannin (flesh coloured) was filtered, washed with brine solution and dried *in vacuo*. The dry solid was powdered and extracted with alcohol. Almost all of it went into solution. After distilling off as much alcohol as possible, the solution was treated with excess of ether. The flesh coloured precipitate was filtered and washed with ether. Further purification was effected by dissolving it again in alcohol and reprecipitating with ether. Thus water-soluble and ether-soluble impurities were removed. The ether solution contained small quantities of substances including probably catechin<sup>3</sup> and giving green colour with ferric chloride solution. But they were not further studied.

*Methylation.*—The purified kino (5 g.) was dissolved in alcohol (50 c.c.), dimethyl sulphate (5 c.c.) added and the mixture shaken well. To this caustic potash solution (3 g. in 3 c.c. water) was added in one lot and the mixture shaken vigorously. It became hot rapidly and the reaction had to be controlled by cooling under the tap. When it had subsided, the process was repeated using the same amount of dimethyl sulphate and potash. After shaking for about an hour the mixture was filtered and the clear solution was diluted with an equal amount of water. A pale brown amorphous solid separated out (yield, 2.5 g.). It was purified by repeated dissolution in alcohol and precipitation with water. Since the product still gave some colour with ferric chloride in alcoholic solution, it was again

subjected to methylation in the above manner and purified. The dried solid was finally dissolved in acetone and fractionally precipitated with petroleum ether. Some coloured impurities were precipitated first and were removed. Subsequently the methyl ether was obtained as an almost colourless amorphous solid. It now gave no colour with ferric chloride in alcoholic solution and did not dissolve in aqueous alkali.

*Acetylation.*—The purified kino (5 g.) was treated with acetic anhydride (15 g.) and anhydrous sodium acetate (5 g.) and the mixture refluxed on an oil-bath for 5 hours. After cooling, the mixture was poured into ice-water and the acetyl-kino that separated out, was filtered, washed with water and dried. It was then purified by crystallisation from chloroform-alcohol mixture whereby it was obtained as a colourless crystalline powder. To ensure complete acetylation, the acetylated product was boiled again with acetic anhydride and anhydrous sodium acetate for 5 hours. The contents were cooled and poured into ice-cold water. The solid that separated out was crystallised from chloroform-alcohol mixture. The final product was colourless and crystalline, but the shape was not definite when seen under the microscope (yield: 3.0 g.).

*Butea gum.*—The purification of Butea gum and the preparation of methyl and acetyl derivatives of the phlobatannin present in it were carried out exactly in the same manner as given in connection with gum kino. The appearance of the products was just the same.

*Comparison of the phlobatannins.*—The purified phlobatannins from the two sources gave identical colour and precipitation reactions with the following reagents: ferric chloride (aqueous and alcoholic), dark green precipitate; gelatin, flesh coloured precipitate; lead acetate, flesh coloured precipitate soluble in 10% acetic acid; boiling aqueous hydrochloric acid, red precipitate; bromine water, immediate orange precipitate; calcium hydroxide, gelatinous pink precipitate; nitrous acid, immediate brown precipitate; formaldehyde and dilute sulphuric acid with warming, flesh coloured precipitate.

Table I gives a comparison of the analytical data relating to the methyl ethers and acetates. The results obtained by Simonsen are also given in the table for purposes of comparison.

TABLE I

Compound	From Butea gum	From Malabar kino	Values for Malabar kino reported by Simonsen
<i>Methyl ether—</i>			
C % .. ..	60.5	60.5	61.7, 62.3
H % .. ..	5.5	5.9	5.5, 5.8
Methoxyl % .. ..	29.3	28.9	26.7, 26.9
$[\alpha]_D^{30}$ .. ..	204.5°	196.2°	..
<i>Acetate—</i>			
C % .. ..	58.7	58.9	58.3, 58.2
H % .. ..	4.4	4.5	4.9, 4.8
$[\alpha]_D^{30}$ .. ..	174.9°	168.9°	..

SUMMARY

The phlobatannin components of kino gum and Butea gum have been purified and rendered free from water and ether-soluble impurities. By subsequent methylation and acetylation almost colourless methyl ethers and acetates have been obtained. They exhibit marked optical activity thus supporting the idea that the phlobatannins are probably hydroxy-flavan derivatives. A comparison of the properties of the phlobatannins from the two sources and of their derivatives indicates that they are identical.

REFERENCES

1. Simonsen .. *J. C. S.*, 1911, 99, 1530.
2. Russel .. *Chem. Rev.*, 1935, 17, 165.
3. Biggs, Cooper, Hazleton, Nierenstein and Price .. *J. A. C. S.*, 1931, 53, 1504.