

THE COLOURING MATTER OF THE TAMARIND SEED TESTA

BY P. S. RAO

(*Forest Research Institute, Dehra Dun*)

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TAMARIND seed contains nearly 30 per cent. of testa and 70 per cent. of kernel. As a result of the large-scale employment of the kernel flour as a size in the jute and textile industries, vast amounts of the testa are available annually. The testa contains a dyestuff which is used by indigenous dyers for dyeing wool and the shades are said to be all-round fast, comparable with acid and after-chrome dyes.¹ The dyestuff is also regarded suitable for dyeing paper and pulp.² The results of a preliminary chemical investigation of this colouring matter are reported in this paper.

The testa can be removed from the seeds by roasting them on hot sand at 125° to 150° for about 20 minutes, and subsequent pounding. It contains 40 per cent. of water-extractable matter of which 80 per cent. is the dyestuff. The latter comprises about 35 per cent. of phlobatannin, 55 per cent. of depside group of tannins and 10 per cent. of an uncharacterized material.

The phlobatannin has been characterized from its response to various reactions characteristic of the group.³ It undergoes easy acetylation and methylation, yielding almost colourless products.

The depside group of the tanstuff belongs to the catechol class. Its tanning properties are not quite satisfactory, since the leather produced is harsh and highly coloured, and is not considered suitable for shoe uppers. However, in combination with myrobalans, it can be used for tanning heavy hides suitable for sole and suit-case manufacture.

EXPERIMENTAL

Extraction of the testa: isolation of phlobatannin.—The powdered testa (100 g.) was boiled with water (1 l.) for about an hour and a half and filtered through a fine muslin. The residue was similarly extracted 3 times more, in order to complete the extraction. The total extract (about 4 litres) was heated to the boiling point and filtered again. The clear filtrate was made

up to exactly 4 litres, and the total solids in it were estimated, taking an aliquot portion. The rest of the filtrate on standing became opaque and a small amount of a fine solid (No. I) separated as a suspension. After 12 hours the solid was filtered through a fluted filter, since filtration under suction was extremely slow. It was washed with small amounts of cold water, dried first on a steam-bath and then in a vacuum desiccator, and weighed. It was pale brown in colour and was amorphous. It was sparingly soluble in water but readily dissolved in sodium hydroxide or carbonate. In aqueous alcoholic solution it gave a bluish-green colour with ferric chloride. The substance was not further examined.

The clear filtrate after the removal of the above solid was concentrated on a water-bath to about a litre and treated with saturated brine. A flesh coloured precipitate appeared, which was filtered, washed with brine and dried *in vacuo*. The dry solid was powdered and extracted in a soxhlet with alcohol (500 c.c.) which dissolved it almost completely. After concentrating the solution to half its volume, excess of ether was added. The precipitate that separated was further purified by redissolution in alcohol and subsequent reprecipitation with ether. The solid thus obtained (No. II) was filtered, washed with ether and dried in a vacuum desiccator.

All the filtrates and washings from the above (aqueous, alcoholic and ethereal) were mixed together and heated on an electric water-bath to drive off the organic solvents. The aqueous solution was reddish yellow in colour. With ferric chloride it produced a green colour which changed into violet red on the addition of sodium bicarbonate, indicating the presence of compounds with catechol nucleus. It gave tests for the dépside group of tannins, which were estimated quantitatively according to the A.O.A.C. Tentative Method of Analysis.⁴

From four sets of experiments conducted with different samples of the testa, the following results were obtained:—

Total solubles: 38–40% of the testa.

Solid No. I: 4–5% of the testa.

Solid No. II: 10–12% of the testa.

Tannins (Dépside group): 16–18% of the testa.

Solid No. II was flesh coloured and was amorphous. It was soluble in water, alcohol and acetone, forming reddish solutions, and was insoluble in ether, benzene and chloroform. In sodium hydroxide it dissolved forming deep-red solutions. In 0.5 per cent. solution it responded to all the reactions characteristic of phlobatannins.³

Reagent	Result
Alcoholic ferric chloride	.. Dark-green precipitate
Aqueous ferric chloride	.. " "
Gelatine	.. Dirty-white precipitate
Lead acetate	.. Pinkish precipitate soluble in acetic acid
Boiling dilute hydrochloric acid (phlobaphene reaction)	Red precipitate
Bromine water	.. Immediate heavy yellow precipitate
Calcium hydroxide	.. Pinkish colour with a precipitate
Sodium sulphite	.. Light pink colour with a precipitate
Formaldehyde and hydrochloric acid	.. Precipitate on warming
Nitrous acid	.. Immediate brown precipitate
Copper sulphate	.. Faint green precipitate
Copper sulphate and ammonia	.. Heavy brownish-green precipitate
Aqueous ammonia	.. Solution darkens slowly
Potassium dichromate	.. Brown precipitate
Potassium ferricyanide and ammonia	.. Orange-red colour
Hide powder	.. Absorbed
Shavings of sheep skin	.. Tanned

Alternatively the phlobatannin could also be isolated in the form of phlobaphene from the aqueous liquor left after the removal of solid No. I, by the addition of mineral or organic acids in such a quantity as to bring down the pH to between 2.8 and 3.2. In this way, the phlobaphene was obtained as an orange-red precipitate sparingly soluble in water but freely soluble in alkalis.⁵

Acetylation of the phlobatannin.—The purified phlobatannin (5 g.) was treated with acetic anhydride (15 g.) and anhydrous sodium acetate (10 g.), and the mixture was gently boiled under reflux on an oil-bath for 4 hours. It was then cooled and poured over crushed ice and stirred well. The acetyl derivative that separated was filtered, washed and dried. In order to ensure complete acetylation, this product was boiled again for 4 hours with acetic anhydride and anhydrous sodium acetate. The acetate appeared to undergo some decomposition when boiled with hydroxy solvents like alcohol and acetic acid. It was, therefore, purified by dissolving in the minimum amount of acetic anhydride and treating with an equal amount of absolute alcohol, when the substance separated out during the course of a day or two as an almost colourless solid, which exhibited no definite crystalline structure. The yield was 2.5 g. The substance did not melt or decompose below 300° (Found in the sample dried at 110° *in vacuo*: C, 60.0; H, 4.5%). Its optical rotation in glacial acetic acid was determined, since in alcohols and acetone it dissolved sparingly. Even with glacial acetic acid, the solution used to turn brownish red, and so the readings had to be taken in a dilute solution (0.25 per cent. concentration). α_D^{30} was found to be +140°.

Methylation of the phlobatannin.—The purified material (5 g.) was dissolved in alcohol (50 c.c.) and treated with dimethyl sulphate (5 c.c.). A 50 per cent. solution of caustic potash (5 c.c.) was added in two instalments with vigorous shaking after each addition. The mixture became hot rapidly and had to be cooled under the tap. When the vigour of the reaction subsided, the process was repeated using the same amount of dimethyl sulphate and alkali. After shaking for about an hour, the mixture was left overnight, filtered and then diluted with an equal amount of water. A pale-brown amorphous solid separated out. To ensure complete methylation the solid was filtered, dissolved in alcohol and treated again with dimethyl sulphate and alkali, as before. The remethylated product was pale brown in colour. For purification it was dissolved in acetone and the solution treated with petroleum ether in drops till it became opalescent. Some coloured impurities were precipitated first and they were removed by filtration. After some time or on the addition of a little more petroleum ether, the methyl phlobatannin separated out as an almost colourless amorphous solid. It gave no colour with ferric chloride in alcoholic solution and did not dissolve in aqueous alkali. It was easily soluble in alcohols, acetone, acetic acid and chloroform, but was sparingly soluble in petroleum ether and benzene. The yield of the pure compound was 1 g. (Found in the sample dried at 110° *in vacuo*: C, 66.3; H, 6.1; OCH₃, 30.6%). Its optical rotation in chloroform solution (0.5 per cent. concentration) was taken and α_D^{20} was found to be +130°. On heating it sintered at about 255° and decomposed at 283° to 285°.

SUMMARY

The tamarind seed testa contains about 32 per cent. of tannins of which 35 per cent. is phlobatannin, the rest being mostly catechol tannin. The phlobatannin yields almost colourless methyl and acetyl derivatives which exhibit marked optical activity, supporting the idea that phlobatannins are probably hydroxy flavan derivatives.

REFERENCES

1. Anon. .. *Jour. Sci. and Ind. Res.*, 1942, 1, 60.
2. Puntambekar, S. V., and Batra, P. C. .. *Indian Forest Leaflet*, No. 44, 1943.
3. Russel, A. .. *Chem. Rev.*, 1935, 17, 165.
4. *Official and Tentative Methods of Analysis of the Assn. of Official Agricultural Chemists*, 3rd Ed., 1930, 155.
5. Krishna, S. .. *Ind. Patent*, 1945, No. 32223.