

WAX FROM *BUTEA FRONDOSA* FLOWERS

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Butea frondosa flowers are well known for their use as a dye-stuff and they are also said to possess medicinal properties. For our studies on these flowers we had occasion to collect them in large quantities during the last three years and subject them to a preliminary treatment to remove the fatty and waxy matter. We found that light petroleum ether removes the waxy matter completely along with some chlorophyll and on further purifying the petroleum ether extract a colourless solid wax (yield 0.75% and m.p. 73-76°) was obtained. However during the last season we used for the preliminary purification carbon tetrachloride in the place of light petroleum ether. On further purifying the extract a colourless wax having the same physical and chemical properties as the previous one was obtained in 0.35% yield. This clearly indicated the existence of a definite waxy matter (m.p. 73-76°) in the flowers, though the yield might vary according to the method adopted or the ripeness of the flowers and seasonal variations.

The unsaponifiable matter of the wax consisted mostly of myricyl alcohol and a very small quantity of a substance probably belonging to the steroid group and giving a bluish-green colour in Liebermann-Burchard reaction. The composition of the acid part seems to be interesting since it was composed mostly of higher saturated acids. The quantities of acids obtained were too small to be separated by fractional distillation and hence crystallisation methods were adopted to separate and characterise them. By repeated fractional crystallisations from different solvents three definite fractions (1) m.p. 76-78°, M.W. 380, (2) m.p. 72-74°, M.W. 350, (3) m.p. 62-64°, M.W. 275 were obtained. From the melting points and the mean molecular weights of these fairly definite fractions, it can be seen that the fraction (1) may be a mixture of cerotic and lignoceric acids, the fraction (2) may be a mixture of arachidic and lignoceric acids and the fraction (3) that of palmitic and stearic acids.

Manjunath *et al*¹ working on the *Butea frondosa* seed oil obtained these higher saturated acids and found it impossible to separate them completely and drew their conclusions from the melting point—molecular weight curves

of mixtures of pure acids. They obtained two definite fractions, in addition to other acids, one melting at 74.5-75.5° with a M.W. 253 and the other melting at 77.5-79° with a M.W. 383 and suggested that they might be eutectic mixtures of equimolecular proportions of behenic and lignoceric, lignoceric and cerotic acids respectively. The existence of the same acids in the flower wax and in the seed oil is highly interesting.

Experimental

Isolation of the Wax.—Several kilograms of the flowers were obtained from the local market, ground into coarse powder and kept well preserved in stoppered bottles for subsequent work. About 5 k.g. of the powder were extracted with light petroleum ether for about 30 hours in a big Soxhlet extractor in batches of 600 g. The solvent was completely removed by distillation and a green greasy solid mass was finally obtained. It looked like a mixture of chlorophyll and a waxy substance. So it was extracted in the cold with acetone and filtered. Only the chlorophyll went into solution leaving the wax on the filter. This was further extracted several times with acetone until the wax was free from the green chlorophyll. Finally it was crystallised from boiling alcohol and obtained as a colourless solid in an yield of 0.75%. It melted at 73-76°.

In subsequent experiments about 5 k.g. of the powder were extracted just as before using carbon tetrachloride. The removal of chlorophyll and other colouring matter (carotenoids) presented considerable difficulty, most of the solvents dissolving the wax as well as the colouring matter. The purification was only partial with acetone. The method adopted for the final purification of the wax which was coloured was first to dissolve the coloured wax in a little CCl_4 , the minimum quantity of solvent being used. Then excess of alcohol was added when the wax was precipitated. This was filtered when the colour passed into the filtrate and the wax was left much lighter in colour. Repetition of this process yielded a pure and almost colourless material melting at 73-76° in an yield of 0.35%.

The wax was sparingly soluble in acetone, chloroform, carbon tetrachloride and cold alcohol. It however dissolved in hot alcohol and when cooled separated in the form of a jelly-like mass which could be filtered under suction. It had the following properties:

Specific Gravity	..	0.98
Saponification Value	..	40.8
Acid Value	..	6.2
Iodine Value	..	1.2
Unsaponifiable Matter	..	70.0%

Unsaponifiable Matter.—The wax was dissolved in a small quantity of benzene and heated with semi-normal alcoholic potash for about 15 hours. The contents were mixed with pumice stone, and the solvents were distilled off and finally they were dried on a water-bath. The dried material was extracted with petroleum ether and acetone successively in a Soxhlet extractor to remove the unsaponifiable matter. The first solvent completely removed the unsaponifiable matter leaving nothing for acetone to extract. This method of extraction was found necessary since the soap formed an emulsion with water and it was found impossible to extract it with petroleum ether or ether.

The unsaponifiable matter consisted of some colourless crystalline material and coloured resinous matter. It was dissolved in excess of hot alcohol and on cooling a colourless crystalline substance was precipitated leaving the filtrate coloured. It was filtered under suction and was found to melt at 80–82°. The chloroform solution of it did not give any colouration with concentrated sulphuric acid and no colouration was produced in Liebermann-Burchard reaction indicating the absence of sterols in it. It was sparingly soluble in acetone, chloroform, ether and cold alcohol. However it readily dissolved in boiling ether and alcohol depositing needle-shaped crystals on cooling. Finally it was recrystallised from ether and it melted at 83–85°. The mixed melting point of this substance with an authentic sample of myricyl alcohol did not exhibit any depression. Finally the whole fraction m.p. 80–82° was boiled with acetic anhydride and anhydrous sodium acetate for 3–4 hours and the contents were thrown into a large excess of water. The precipitated solid was filtered and crystallised from boiling alcohol and ether successively when it was obtained in the shape of fine needles. It melted at 70–71° and did not show any depression in the melting point when mixed with an authentic sample of myricyl acetate. So this fraction was identified as myricyl alcohol. The highly coloured alcohol mother liquor from which myricyl alcohol had been crystallised was treated with bone-char when a yellow solution was obtained. On distilling off the alcohol a small quantity of an yellowish sticky mass melting at 70–80° was obtained. It was dissolved in a small quantity of chloroform and alcohol was added to it till there was slight turbidity and the mixture cooled in the ice-chest. A white solid mixed with traces of yellow resin precipitated out and it was filtered. The precipitate when dissolved in chloroform and a few drops of concentrated H_2SO_4 added, produced orange-red colour in the chloroform layer and the solution exhibited intense green fluorescence. On standing for about half an hour the sulphuric acid layer took up the colour and the chloroform layer became violet. To the chloroform solution of the substance about 20 drops of acetic anhydride were added and the

contents boiled and cooled. Subsequently a drop of concentrated H_2SO_4 was added to it and shaken when slowly a blue solution changing immediately to bluish-green and finally to bright-green was produced. The colour faded to dull-brown in about two hours. When the substance was acetylated as usual with acetic anhydride and anhydrous sodium acetate no crystalline compound could be obtained. However the crude product of acetylation also gave the above colour reactions. The mother liquor from which the above solid was obtained, was distilled off completely when a semisolid coloured mass was left behind. However it gave the usual sterol colour reactions and in Liebermann-Burchard reaction a play of colours was obtained from pink to green.

The Fatty Acids.—After the unsaponifiable matter was extracted, the soap was decomposed in the usual way by boiling with dilute sulphuric acid to liberate the acids. The acids were separated into saturated and unsaturated fractions by Twitchell's² lead salt method. The unsaturated acid fraction which was negligible in quantity was rejected and the saturated solid acids were dissolved in boiling alcohol and decolorised by treating the solution with a pinch of animal charcoal. The alcohol solution was slowly concentrated and cooled in the ice-chest when a considerable amount of a colourless solid separated out. On further concentration and subsequent cooling no more solid could be separated from the alcohol solution. The solid was dissolved in a small quantity of ethyl acetate, concentrated and cooled in ice for about four hours when a fraction which softened at 72° was obtained. It was crystallised four times from ethyl acetate and subsequently from alcohol when finally it melted at 76–78°. The molecular weight of this fraction was determined by titrating it with standard potash solution and an average of two experiments gave a value of 380. This may be a mixture of cerotic and lignoceric acids. The ethyl acetate mother liquor did not deposit any more solid on concentration and subsequent cooling. A small amount of 95% alcohol was added to it and cooled in the ice-chest. A solid fraction was obtained which started melting at 69° and finally melted at 74°. This was repeatedly purified by the above process when finally a fraction was obtained which melted at 72–74° and further treatments did not alter the melting point. The molecular weight of this fraction was 350 and probably this may be a mixture of arachidic and lignoceric acids. Finally the mother liquors from which the fraction melting at 72–74° was precipitated and the original alcohol mother liquor were united and the solvent distilled off when a small amount of a solid was obtained. Further fractionation of this solid was tried through different solvents but no definite fraction could be obtained. This melted at 62–64° and its molecular weight (mean of 3 values) was 275. This may be stearic and palmitic acid mixture.

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Summary

A colourless wax has been isolated from the flowers of *Butea frondosa* and its physical and chemical properties are described. The unsaponifiable matter consists mainly of myricyl alcohol along with small quantities of steroids. The composition of the saturated fatty acid mixture is very similar to that found in the seed oil.

REFERENCES

1. Katti and Manjunath .. *J. I. C. S.*, 1929, **6**, 839.
Krishna Rao and
Manjunath .. *Ibid.*, 1935, **12**, 611.
2. Twitchell .. *Ind. Eng. Chem.*, 1921, **13**, 806.