CHEMICAL EXAMINATION OF THE BARK OF *ALANGIUM LAMARKII* THWAITES. ISOLATION OF THE ALKALOID ALANGINE

BY DHARAM BAL PARIHAR AND PROF. SIKHIBHUSHAN DUTT
(*Chemistry Department, Delhi University*)

Received January 26, 1946

Alangium Lamarkii or Ankula as it is known in Bengali and Sanskrit, and Akola in Hindi, is a small handsome evergreen tree belonging to the Natural Order of Alangiaceæ. It is met with throughout India, often growing wild, but sometimes cultivated as an ornamental garden plant for the beautiful, narrow, oblong and prominently reticulated leaves and white wax-like glossy flowers. It is particularly abundant in Chota Nagpur, Orissa, Andhra districts, Central Provinces, United Provinces and South-Eastern Punjab.

The plant is highly medicinal. According to Kirtikar and Basu,[1] the root is acrid, bitter, slightly pungent, heating, anthelmintic, alterative. It cures erysipelas, biliousness, inflammations and snake bites and acts like a fish poison. The bark is emetic, alexipharmic and cures cough, rheumatism, pain, inflammations, biliousness, diseases of the blood, hydrophobia, rat-bite, lumbago, dysentery, diarrhœa and worms. The seeds are cooling, aphrodisiac, indigestible, tonic, nutritive and laxative. They cure burning sensations, consumption, hæmorrhage, biliousness, erysipelas, cough and loss of appetite. They have also a reputation in the cure of leprosy.

The seeds of the plant have already been worked out by Bhargava and Dutt,[2] who isolated from them an interesting sterol having a molecular formula $C_{42}H_{84}O_7$, which they named 'alangol'. Very little fixed oil was found in the seed and no other constituent could be detected.

The bark of the plant has not yet been properly worked by anyone. Dymock[3] has reported the presence of an uncrystallisable alkaloid which could not be obtained in a pure form. According to him all the salts of the base are uncrystallisable. On ignition, the platinum salt gave 20·70% of platinum from which the molecular weight of the base was found to be 265·9. No further work has been done by any one on this subject.

The present authors working on the bark of the plant have been able to isolate an alkaloid crystallising in glistening, yellow prisms and melting at

205–08° C. The molecular formula of the substance which has been named 'alangine' was found to be $C_{19}H_{25}O_2N$, and it behaved like a mono-acid base with one methoxy group. There was an indication of an alcoholic hydroxy group due to the formation of acetyl and benzoyl derivatives, but they did not give good analytical results.

Alangine is strongly basic in nature and forms well-defined and crystalline hydrochloride, iodide, oxalate, tartrate, nitrosate and iodomethylate. It is a tertiary base but does not contain any $> N-CH_3$ group as by Herzig and Meyer's method no indication of such a group in the molecule was obtained.

Alangine is present in the bark of *Alangium Lamarkii* to the extent of 0·1%. The bark besides containing alangine also contains a fair proportion of colouring matters, potassium nitrate, gum, etc. Fresh bark has been found to contain a greater proportion of alangine than the bark which has been stored for some time. The chemical properties and reactions of alangine correspond to no known alkaloid. So it must be a new compound.

EXPERIMENTAL

Extraction of the bark with different solvents

20 gm. of the finely powdered bark were extracted with different solvents in a Soxhlet's apparatus, the solvent evaporated and the residue dried to a constant weight. The percentage of the extract by each solvent is given below:—

Water	15·05
Alcohol	13·98
Acetone	8·22
Chloroform	2·96
Ethyl acetate	3·01
Benzene	1·15

In each of the above extracts the reactions of an alkaloid was given by all the alkaloid reagents. The extracts were also extremely bitter in taste.

Isolation of the alkaloid

200 gm. of the air-dried powdered bark were repeatedly percolated with acidulated water (0·5% HCl) at the ordinary temperature until the last extract obtained did not give any appreciable precipitate with Dragendorff's reagent. The extract gave the following reactions with various alkaloid reagents:—

(1) Dragendorff's reagent	Thick orange precipitate.
(2) Wagner's reagent	Thick brown precipitate.
(3) Meyer's reagent	Deep yellow precipitate.
(4) Phosphotungstic acid	Bright yellow precipitate.
(5) Phosphomolybdic acid	Thick yellow precipitate.
(6) Platinic chloride	Yellow precipitate.
(7) Auric chloride	Yellow precipitate.
(8) Tannic acid	Buff coloured precipitate.
(9) Picric acid	Yellow crystalline precipitate.
(10) Chromic acid	Yellow-brown precipitate.
(11) Sodium carbonate	Yellow precipitate (Free alkaloid).
(12) Conc. Sulphuric acid	Light brown colouration.
(13) Luchini's reagent	Yellow-brown-violet-green.
(14) Erdmann's reagent	Violet-orange.
(15) Conc. Nitric acid	Light violet.
(16) Frode's reagent	Violet, changing to yellow.

The total extract was neutralised with dilute sodium carbonate and the resultant thick yellow precipitate filtered off, washed with water and dried in the air. It was then extracted with hot ammoniated alcohol (0·5%) and the extract after neutralisation with acetic acid, evaporated to a syrup under reduced pressure. The syrupy material was then extracted with ethyl acetate, and the ethyl acetate extract after concentration, precipitated with a mixture of ether and petroleum ether (2:1). The resulting granular yellow precipitate was filtered off, washed with petroleum ether and then further purified by repeatedly dissolving it in chloroform and reprecipitating with ether. The purified alkaloid which was thus obtained as a bright yellow powder was finally crystallised from a mixture of chloroform and ether and the process repeated a number of times until no further rise in the melting point was noticed. The base was thus obtained in the form of glistening yellow elongated prisms melting at 205–08° C. with decomposition.

It is sparingly soluble in cold water but more so in the hot. It is easily soluble in alcohol, ethylacetate, acetone, chloroform, carbon disulphide and pyridine but is quite insoluble in benzene, ether and petroleum ether. An aqueous solution of the alkaloid is extremely bitter to taste and is faintly basic towards litmus, phenolphthalein and methyl-orange. The substance is optically active, showing $[\alpha]_D^{22^\circ} = +9^\circ$ in alcohol. A microphotograph of the alkaloid is given showing its finely crystalline form. Found: $C =$

75·92, 76·02%; H = 8·54, 8·48%; N = 4·75, 4·82% (Duma's); 4·47, 5·04% (Kjeldahl); M.W. = 296,304,297 (Rast's Camphor method); 307,297 (Ebullioscopic in Chloroform); 297·6, 292·3 (ignition of the chloroplatinate); 290·6, 304·0 (ignition of the Chloroauriate); $C_{19}H_{25}O_2N$ requires C = 76·25%, H = 8·36%, N = 4·68%; M.W. = 299.

The alkaloid contains one methoxyl group in the molecule. (Found: OCH_3 = 10·45, 10·25, 10·42 by Zeissel's method. $C_{18}H_{22}ON\ OCH_3$ requires OCH_3 = 10·36%.) The absence of N-methyl was confirmed.

Preparation of the salts of the alkaloid

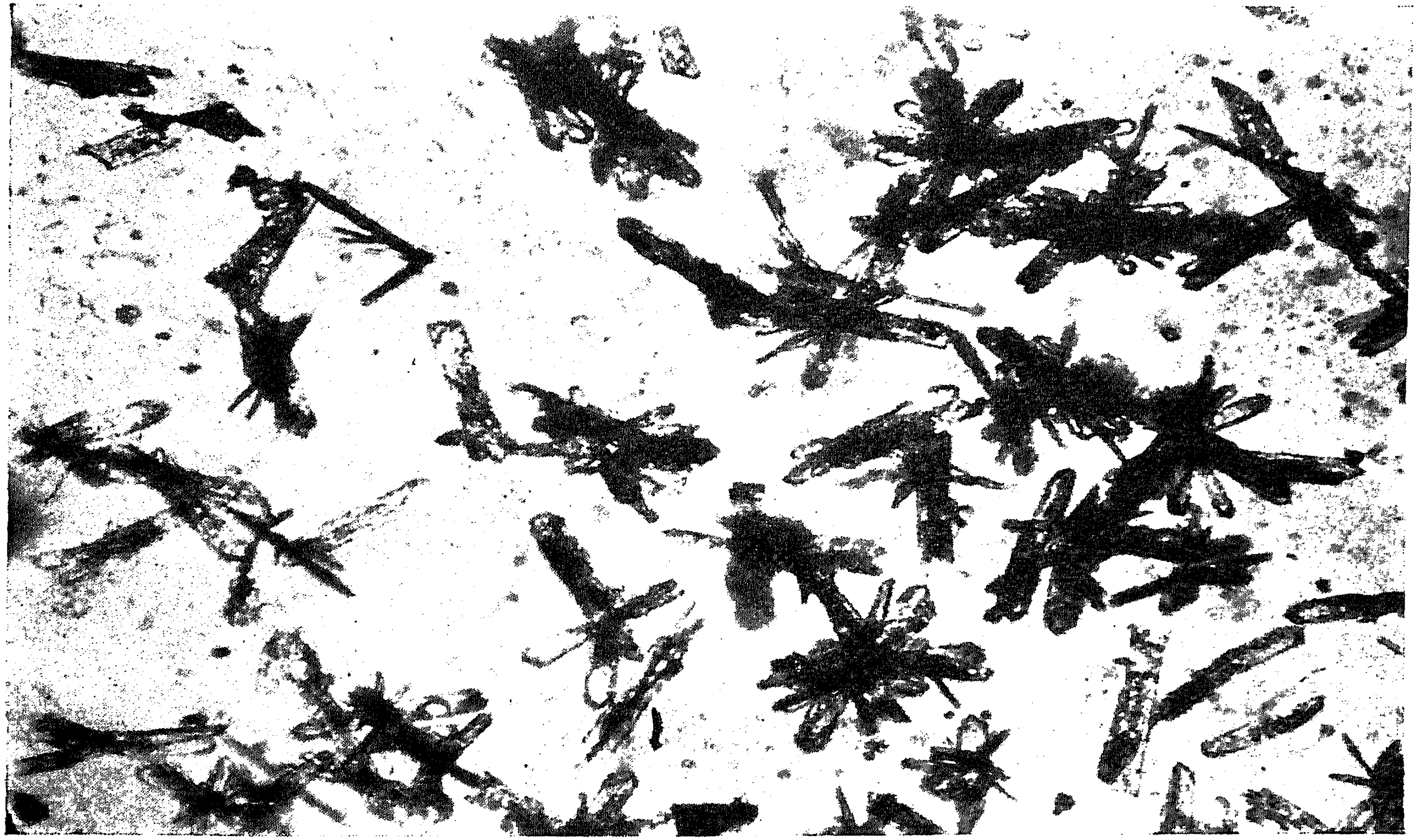
Alangine hydrochloride.—The hydrochloride of the base was prepared by dissolving it in alcohol and treating with a slight excess of warm alcoholic hydrogen chloride. On cooling and adding a little ether to the solution, the hydrochloride was obtained as yellow crystalline prisms, melting at 264° C. It is easily soluble in water and ordinary organic solvents except benzene, ether and petroleum ether. (Found: Cl = 9·94; $C_{19}H_{25}O_2N.HCl$ requires Cl = 10·58 per cent.)

Alangine sulphate.—This was obtained by adding alcoholic sulphuric acid to an alcoholic solution of the base, and diluting the mother-liquor slightly with ether. The sulphate came down as a light yellow powder melting at 118° C. The salt is sparingly soluble in cold water but is readily soluble in alcohol, chloroform and acetone. It is insoluble in ether, benzene and petroleum ether. (Found: S = 4·59, 4·71; $(C_{19}H_{25}O_2N)_2.H_2SO_4$ requires S = 4·60%.)

Alangine nitrate.—This was obtained in a similar way as the hydrochloride and the sulphate, from alangine and alcoholic nitric acid. It is a yellow crystalline powder melting at 176° C. The properties of this substance are similar to those of the other inorganic salts.

Alangine iodide.—To a hot aqueous solution of the chloride was added a concentrated solution of potassium iodide. The iodide separated as a deep yellow crystalline precipitate. It was recrystallised from ether-alcohol mixture in the form of yellow prisms melting at 178° C. with decomposition. The substance is sparingly soluble in water but readily in alcohol. It is insoluble in ether and petrol ether. (Found: I = 29·38; $C_{19}H_{25}O_2N.HI$ requires I = 29·74%.)

Alangine acetate, tartrate and oxalate.—These were prepared by the action of alcoholic acetic, tartaric and oxalic acids on alcoholic solutions of alangine. They are all yellow, crystalline substances with properties



similar to those of the chloride. Alangine acetate melts at 202° C., tartrate at 220° C. and oxalate at 89° C.

Alangine picrate.—To a solution of the base in dilute hydrochloric acid was added a saturated aqueous solution of picric acid when a light-yellow, crystalline powder came down. This was recrystallised from ether-alcohol mixture in glistening flakes, melting at 84° C. It is soluble in alcohol, chloroform, ethyl acetate and acetone and sparingly in benzene. It is insoluble in ether and petrol ether. (Found: $N = 10 \cdot 34$; $C_{25}H_{28}O_9N_4$ requires $N = 10 \cdot 60\%$.)

Alangine-iodomethylate.— To a solution of the base (1 gm.) in chloroform (3 c.c.), methyl iodide (1 c.c.) was added and the mixture strongly cooled. On allowing to stand for about two hours, a deep yellow crystalline substance separated out. This was filtered, washed with chloroform and dried under vacuum at room temperature (21° C.). It melts at 201° C. with decomposition. (Found: $I = 28 \cdot 53$; $C_{20}H_{28}O_2NI$ requires $I = 28 \cdot 79\%$.)

The quaternary salt is very soluble in water and alcohol, but the solubility decreased in the order—ethyl acetate, chloroform, acetone and benzene. It is completely insoluble in ether and petrol ether.

SUMMARY AND CONCLUSION

1. From the bark of *Alangium Lamarkii* Thwaites, a new alkaloid has been obtained crystallising in long yellow glistening prisms, m.p. 205—08° C. The molecular formula of the alkaloid has been found to be $C_{19}H_{25}O_2N$. This has been named " ALANGINE ".

2. The alkaloid has been found to be a monoacid base containing one methoxy group but no $> N-CH_3$ group.

3. The alkaloid which is dextrorotatory easily gives crystalline salts with organic and inorganic acids and the hydrochloride, sulphate, nitrate, iodide, acetate, tartrate, oxalate, picrate and iodomethylate have been prepared and described.

REFERENCES

1. Kirtikar and Basu .. *Indian Medicinal Plants*, **1**, 630.
2. Bhargava and Dutt .. *Proc. Ind. Acad. Sci.*, 1942, **16**, 328.
3. Dymoch .. *Pharmacographia Indica*, 1893, **2**, 164.