CHEMICAL EXAMINATION OF THE SEEDS OF *ALANGIUM LAMARKI*, THWAITES

Isolation of Alangol

BY PRITHVI NATH BHARGAVA AND SIKHIBHUSHAN DUTT
(From the Chemical Laboratory, Allahabad University, Allahabad)

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Alangium Lamarki, Thwaites, known in Hindi as "Akola" and in Sanskrit and Bengali as "Ankula" is a small handsome evergreen tree belonging to the Natural Order Cornaceæ. It grows quite well in the sub-Himalayan tract and also in Central and Southern India. The seeds of the plant are highly medicinal and have been described by Kirtikar and Basu[1] as cooling, tonic, nutritive and useful in the case of burning sensation in the body and also in consumption and hæmorrhage. They have also a reputation in the cure of leprosy. Besides the seeds, the bark and the root of the plant have highly medicinal properties, but they will be the subject of a future communication.

The raw fruits have a deep crimson pericarp which on drying assumes a dark-brown, in fact almost black colour. The dried seeds are 10–15 mm. in length and 5–8 mm. in diameter and are not unlike small hazelnuts in appearance. On breaking off the outer shell, the inner kernel is found to be white or pale cream coloured, very closely resembling the kernel of groundnut, but having a peculiar characteristic smell of the drug.

The most surprising fact about the seeds is that they do not contain any appreciable quantity of fixed oil. On extraction of the crushed kernels with benzene, a colourless crystalline substance having all the properties of a sterol is ultimately obtained, melting at 296° C. This substance has consequently been named "alangol". The molecular formula of this compound from the analytical data and its molecular weight by Rast's method has been found to be $C_{42}H_{84}O_7$. From the formula and also its very high melting point, it is undoubtedly the most complicated sterol that has yet been discovered. The substance has been found to contain an alcoholic hydroxy group, since it yields a monoacetyl, a monobenzoyl and a monophenyl urethane derivative respectively on treatment with acetic anhydride, benzoyl chloride and phenylisocyanate. About the nature of the remaining six atoms of oxygen in the molecule, no indication has as yet been found. A digitonide of the sterol has also been prepared.

Alangol is present in the seeds of *Alangium Lamarki* to the extent of 0·05 per cent. (0·08 per cent. of the kernels). The kernels of the seeds besides containing alangol, also contain a large proportion of starch, small amounts of sugars, tannins, traces of protein matter, but no alkaloids, glucosides, fats or bitter principles. Fully mature and ripe seeds have been found to contain a much greater proportion of alangol than unripe or immature seeds. It is interesting to note in this connection that in the Ayurvedic system of medicine, only the ripe seeds have been prescribed.

The pericarp or shells of the seeds have also been examined. They have been found to contain nothing that is interesting from the chemical point of view. They only contain tannins, sugars and colouring matters besides cellulose and inorganic substances.

Experimental

Shells and kernels of the seeds.—10 kilos of the authentic ripe seeds were procured from the Punjab Ayurvedic Pharmacy, Amritsar, and the kernels extracted from them by the laborious process of shelling and picking. The kernels weighed 71·4 per cent. of the whole seeds, the remainder being the shells. Both shells and kernels on incineration left a greyish-white ash, which was analysed qualitatively with the following results:

Shell ash (8·5%).—Water-soluble portion (56·3%) contains chloride, sulphate, carbonate, sodium and potassium. Water-insoluble portion (43·7%) contains calcium, magnesium, silica, alumina, iron and phosphate.

Kernel ash (3·03%).—Water-soluble portion (76·9%) contains chloride, sulphate, carbonate, potassium, sodium and magnesium. Water-insoluble portion (23·1%) contains calcium, magnesium, iron and phosphate.

Preliminary chemical examination of the kernels.—The shell-free kernels were pulverised in a grinding machine and the product in 20 gm. lots was extracted with various organic solvents in a Soxhlet's apparatus. The solvents were subsequently evaporated. The results are indicated below:

Ether extract (0·61%).—Yellowish sticky substance.

Petroleum ether extract (0·38%).—Similar to the ether extract.

Benzene extract (1·04%).—Dark brown crystalline substance containing mainly alangol.

Alcohol extract (15·56%).—Dark reddish brown sticky substance containing embedded crystals of alangol. Contains sugars and tannins also.

Chloroform extract (3·35%).—Orange coloured sticky substance, partially solidifying to a crystalline mass on standing.

Ethyl acetate extract (2·46%).—Reddish brown crystalline solid containing mostly alangol together with some colouring matters.

Aqueous extract (31·31%).—Dark brown syrupy substance containing mostly tannins and sugars.

Isolation of alangol.—3·5 Kilos of the coarsely powdered kernels of seeds were extracted with boiling benzene in a five litre extraction flask fitted with a reflux condenser. The extraction was repeated with fresh benzene for a number of times until a small portion of the extract on complete evaporation did not give any crystalline residue. The combined extracts (10 litres) were distilled off to about one-tenth the original volume and allowed to cool, when large quantities of a brown crystalline substance were deposited. These were filtered off, washed with a little petroleum ether and dried in the steam oven when the substance became considerably reduced in volume, apparently due to the loss of benzene of crystallisation. Further quantities of the substance were obtained by evaporation of the mother liquors. The total amount of the crude material thus obtained from 7 kilos of the kernels yielded by 10 kilos of the whole seeds weighed 10·4 grams, thus giving an yield of 0·1 per cent. on the weight of the whole seeds. This was dark borwn in colour and melted indefinitely at 264–282° C. For purification, the substance was boiled under reflux for four hours with a 20% aqueous solution of caustic soda which removed most of the colouring and resinous matters. The residue was washed with hot water until free from alkali, dried and repeatedly crystallised from methyl alcohol with the addition of animal charcoal, when finally it was obtained in long colourless cotton-like needles meltimg at 296° C. The yield of the perfectly pure substance was 5·2 gm., thus giving an yield of 0·052 per cent. on the weight of the whole seeds.

Alangol crystallises best from 80 per cent. methyl alcohol in glistening needles with one molecule of water of crystallisation which is lost on heating the substance at 110° C. for two hours. It is sparingly soluble in cold methyl or ethyl alcohol, glacial acetic acid, benzene, chloroform and acetone, but dissolves more freely in these solvents in the hot state. In pyridine and nitrobenzene it dissolves very easily in the cold. The substance is almost insoluble in petroleum ether and is quite insoluble in water. In concentrated sulphuric acid in the cold it dissolves with a yellow colour which becomes reddish brown, specially on warming. The solution of the substance in acetic anhydride on treatment with chloroform and a few drops of concentrated sulphuric acid immediately assumes a pink colour which rapidly changes into violet, then blue and finally green. This is a characteristic reaction of all sterols. From concentrated sulphuric acid solution, the substance is

precipitated unchanged on dilution with water. (Found: C = 72·22, 72·13; H = 11·92, 11·62; M.W. by Rast's camphor method = 702; $C_{42}H_{84}O_7$ requires C = 72·0; H = 12·0; M.W. = 700.) $[\alpha]_D^{26°\,c.}$ × 29·7° in chloroform.

Monoacetyl-alangol.—This was prepared in the usual manner by heating alangol with acetic anhydride and a few drops pyridine under reflux for one hour. The substance crystallises from dilute alcohol in colourless needles, which on heating shrink at 256° C. and melt at 265° C. (Found: C = 70·80; H = 11·72; $C_{44}H_{86}O_8$ requires C = 71·15; H = 11·59 per cent.)

Monobenzoyl-alangol.—This was prepared by heating under reflux a mixture of alangol (0·5 gm.), pyridine (20 c.c.) and benzoyl chloride (5 c.c.) for one hour. The product was poured into water and the colourless precipitate thus obtained was washed with water, dilute sodium carbonate solution and again with water. It was finally crystallised from dilute alcohol in colourless prisms melting at 276° C. (Found : C = 72·73; H = 11·35; $C_{49}H_{38}O_8$ requires C = 73·13; H = 10·94 per cent.)

Alangol-monophenylurethane.—This was prepared by allowing a mixture of alangol (0·5 gm.), phenylisocyanate (1 gm.) and dry benzene (200 c.c.) to stand at the ordinary temperature in a carefully closed flask for a week, when from the clear solution, a part of the phenylurethane derivative crystallised out. More of the substance was obtained by distilling off the solvent to one-tenth the original volume and allowing the mother liquor to crystallise during another week. The combined product was recrystallised from boiling alcohol in glistening prisms, melting at 242° C. (Found: N = 1·6; $C_{42}H_{83}O_6O.\ CONHC_6H_5$ requires N = 1·7 per cent.)

Alangol-digitonide.—This was prepared by heating under reflux a mixture of alangol (0·5 gm.) and digitonin (0·5 gm.) dissolved in alcohol (150 c.c.) for three hours. On cooling the digitonide crystallised out in glistening prisms melting at 270–273° C. (Found: C = 6·74; H = 9·80; $C_{42}H_{84}O_7.\ C_{55}H_{94}O_{28}$ requires C = 61·19; H = 9·35 per cent.)

Summary and Conclusion

1. From the kernels of the seeds of *Alangium Lamarki*, Thwaites, a sterol has been obtained crystallising in colourless silky needles and having a molecular formula $C_{42}H_{84}O_7$. This has been named "alangol".

2. The sterol has been found to contain an alcoholic hydroxy group, and a number of derivatives of this substance have been obtained.

REFERENCE

1. Kirtikar and Basu .. *Indian Medicinal Plants*, p. 638.