

KANUGIN, A CRYSTALLINE COMPONENT OF THE ROOTS OF *PONGAMIA GLABRA*

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OF the different parts of *Pongamia glabra*, the seeds and the fixed oil derived from them are well known for their medicinal properties. Two crystalline compounds responsible for these properties have so far been isolated. The constitution of one of them, karanjin, has been definitely established and it has been obtained by synthesis also.¹ The other compound known as pongamol was only recently discovered and its study is still incomplete.² Various other parts of the tree have also been used for medicinal purposes in India from very early times. Among them the roots seem to possess antiseptic properties. The juice obtained from them has been used for cleansing foul ulcers and closing fistulous sores and is given internally in gonorrhoea and urethritis. They have therefore been examined and some of the results are reported in this communication.

A preliminary extraction of the powdered roots with alcohol gave a highly coloured extract which yielded a dark residue on concentration. It showed no tendency to crystallise. However, by extracting it with ligroin much of the coloured matter was left behind and from the solution a poor yield of a colourless crystalline solid was obtained with difficulty. When, however, the material was directly extracted with hot ligroin (*b.p.* 90–110°) the extract was much less coloured. On concentration and treatment with a little ether in order to remove resins and oily matter a mass of almost colourless crystalline solid was obtained. Subsequent extraction of the root powder with alcohol did not yield any definite component. Hence the study of this extract was not made in any detail. Comparative experiments using the entire root and the root bark alone indicated that the above-mentioned crystalline substance was present mostly in the bark. Consequently in all the later experiments this part of the root alone has been employed.

The crystalline compound obtained from the ligroin extract can be easily recrystallised from alcohol-acetic acid mixture and thus rendered pure. It melts at 197–8° and has the molecular formula $C_{19}H_{18}O_7$. It

seems to differ from all known substances. It is definitely different from karanjin and pongamol. It has therefore been given the new name "kanugin" derived from the Telugu name of the tree 'Kanuga'. Derivations from the botanical name of the tree *Pongamia glabra* and the Sanskrit name 'karanja' are already in use, in the case of pongamol, glabrin (the nitrogenous compound present in the seeds)³ and karanjin.

Kanugin is a neutral substance. Since it is insoluble in alkali and gives no colouration with ferric chloride or lead acetate it may not contain any phenolic hydroxyl groups. It however has three methoxyl groups in the molecule and seems to be a completely methylated compound. In this respect it resembles rotenone the chief active principle of the roots of another leguminous plant *Derris elliptica*. However, it does not show the usual rotenone colour reactions. On the other hand it gives a deep red colour by reduction with magnesium and hydrochloric acid thus showing that it belongs to the group of methoxy-flavones.

It is highly significant that while the seed contains a good amount of karanjin and some pongamol, they are absent from the root. It happens not infrequently that the same compound is present in different parts of the same plant though in varying amounts. This is obviously not the case in *Pongamia glabra*. The characteristic differences between the crystalline components of the seed and of the root are given in the following table. However, all the concerned compounds seem to be flavone derivatives.

	Karanjin	Pongamol	Kanugin
M.p.	158°	128°	197°
Mol. formula	C ₁₅ H ₁₂ O ₄	C ₁₈ H ₁₄ O ₄	C ₁₉ H ₁₈ O ₇
Conc. H ₂ SO ₄	Pale yellow soln.; green after 20 min. bluish green after 40 min.	Yellow soln. with green fluorescence; deep emerald green in 5 min.	Yellow soln. with green fluorescence; orange after 10 min. and red after half an hour.
FeCl ₃ colour	Nil	Deep red	Nil
Dil. aq. NaOH	Insoluble	Almost insoluble	Insoluble
Methoxyl	Present	Present	Present
Reduction with Mg+HCl	Orange yellow	Orange red	Deep red
Boric-citric reaction	Negative	Positive	Positive
Taste	Slightly bitter	Less bitter	Not bitter

Experimental

The sample of the roots was obtained from the trees in the Andhra University campus in March. The roots from younger trees were about $\frac{1}{2}$ -1 inch in diameter and were more easily available near the ground surface. The more mature trees yielded roots varying in thickness from

1 to 3 inches. The bigger roots were more easily available in bulk and provided bark more easily. However, no selection was made of the material and it was a composite sample from roots of different sizes. After washing the roots free from soil, the bark was separated from the inner woody portion, dried and powdered.

Extraction with alcohol.—The powdered bark was extracted for ten hours with boiling alcohol. The extract was poured off and a second extraction was made using fresh alcohol for six hours. The combined extract was concentrated by distilling on a water-bath as far as possible and allowed to stand. Since no solid separated even after a number of days, the solution was evaporated from a porcelain basin on a steam-bath and the residue finally dried in a steam oven. The dark pitch-like residue was then extracted with boiling ligroin and the extract which was pale brown in colour evaporated to dryness. The residue was dissolved in alcohol and diluted with ether. On slow and spontaneous evaporation of this solution a light granular solid gradually separated out along with some resin. It was filtered, washed with ether and crystallised from alcohol containing a few drops of acetic acid. Clusters of colourless needles melting at 187° with a little previous sintering were obtained. After one more recrystallisation the melting point rose to $194-95^{\circ}$.

Extraction with ligroin.—The powdered root bark was extracted with hot ligroin three times, heating on a steam-bath for 10, 6 and 6 hours using fresh solvent for each operation. The combined extract was concentrated as far as possible on an oil-bath maintained at $100-10^{\circ}$. The residual dark and viscid liquid (about 100 c.c. from 2 kg. of the powder) was treated with ether (100 c.c.) and crystallisation induced by stirring vigorously with a glass rod and scratching the sides of the flask. A considerable amount of granular solid was formed within about half an hour. After allowing to stand further for three hours it was filtered and washed with ether in order to remove adhering oily and resinous impurities. Crystallisation from alcohol-acetic acid mixture yielded a colourless solid melting at 192° and sintering a few degrees earlier. A second crystallisation from the same solvent gave pure kanugin in the form of fine needles and narrow rectangular plates melting at $197-98^{\circ}$. Further crystallisations did not raise the melting point. The yield of the pure substance was about 0.05% on the weight of the dry bark powder. (Found: C, 63.7; H, 4.7; OCH_3 , 25.6; $\text{C}_{19}\text{H}_{18}\text{O}_7$ requires C, 63.7; H, 5.0; OCH_3 (3), 26.0%. Molecular weight determined by Rast's method : 360, 341 ; $\text{C}_{19}\text{H}_{18}\text{O}_7$ requires mol. wt. 358.)

The compound was sparingly soluble in alcohol and moderately soluble in acetic acid. It was insoluble in dilute aqueous alkali by which it was unaffected even after boiling for 10 minutes. An alcoholic solution gave no colour with ferric chloride or lead acetate. It dissolved in cold concentrated sulphuric acid giving a yellow solution with a faint green fluorescence; the solution turned green after keeping for about 5 minutes, orange after 10 minutes and red after half an hour, the fluorescence becoming less and less apparent. Concentrated hydrochloric acid dissolved the compound producing a yellow solution. On reduction of the alcoholic solution with magnesium powder and hydrochloric acid a bright red colour was produced. A positive result was obtained with Wilson's boric acid test. Kanugin was compared with rotenone using the following reactions:

(1) A small quantity of kanugin was placed on a porcelain bit and a drop of concentrated nitric acid added. The substance was partly charred and the rest dissolved to give a yellow solution. On treating this with a few drops of ammonia no change in colour was observed. Rotenone gives a red solution with nitric acid and the solution turns green or bluish green with ammonia.

(2) A chloroform solution of kanugin (about 2 mg. in 5 c.c.) was mixed with a chloroform solution of thymol (5 c.c. of a 10% solution) and subsequently treated with a few c.c. of concentrated hydrochloric acid containing a trace of nitric acid and well shaken. The chloroform layer was coloured yellow which turned dirty brown after about half an hour. Rotenone gives an olive or bluish green colour in a few minutes.

Summary

A crystalline compound melting at 197-8° and having the molecular formula $C_{19}H_{18}O_7$ has been isolated from the roots of *Pongamia glabra*. It has been named kanugin. It is a neutral body having three methoxyl groups and it differs in its properties from karanjin, pongamol and rotenone.

REFERENCES

1. Seshadri and Venkateswarlu *Proc. Ind. Acad. Sci., A*, 1941, **13**, 404.
2. Rangaswami and Seshadri .. *Ibid.*, 1942, **15**, 417.
3. Rao and Rao .. *Ibid.*, 1941, **14**, 123.