

CHEMISTRY OF PONGAMOL. PART I

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THE discovery of a new crystalline compound from the oil of *Pongamia glabra* was announced in a communication sent to *Current Science*.¹ The remarkably bright colours which it yields with ferric chloride and with concentrated sulphuric acid gave a clue to the existence of this compound in the oil. Compared with karanjin it is a minor component, far more soluble in oils, less bitter and less toxic to fish.² Owing to the difficulties of isolation of the substance in a pure condition and the complexity of its reactions the problem of elucidating its constitution has proved to be difficult and slow in progress. We are therefore presenting in this paper the important results obtained so far.

The results of combustion analysis suggest the formula $C_9H_7O_2$ and a determination of the molecular weight indicates that the molecular formula should be just double this, $C_{18}H_{14}O_4$. This is further supported by the analysis for the methoxyl group and calculation for the weight of the compound containing one methoxyl.

Though from the reaction of the compound with ferric chloride the presence of a phenolic or enolic group is definite, isolation of a derivative in a pure condition has not been possible, since the methyl ether, acetate and benzoate came mostly as liquids in small quantities. The *p*-nitro-benzoyl derivative was obtained tolerably pure and its analysis supported the above formula.

Demethylation of pongamol has given rise to somewhat anomalous results and two products have been obtained by using different demethylating agents. By the action of hydrobromic acid and acetic anhydride and also by the action of hydriodic acid the same compound (I) resulted. Though this gave a slightly low carbon value on analysis, it agreed with the expected value for the simple demethylation product fairly satisfactorily. But the substance behaved extraordinarily in its reactions since it gave no colour with ferric chloride and was insoluble in alkali. With aluminium chloride, however, demethylation proceeded differently and the nor-pongamol (II) so obtained was readily soluble in alkali and gave satisfactory analytical results. It may

be tentatively stated that aluminium chloride brings about a simple demethylation whereas the halogen acids carry the reaction further in a manner which is not at present clear.

By the action of bromine in glacial acetic acid pongamol gave rise to a bromo-derivative which contained four bromine atoms in the molecule ($C_{18}H_{14}O_4Br_4$). It did not give any of the colour reactions of pongamol with ferric chloride or sulphuric acid. At least a portion of the bromine seemed to be held in a loose condition since on boiling the compound with acetone the evolution of bromo-acetone could be noticed. From the analytical results it could be concluded that the resulting compound had the formula $C_{18}H_{13}O_4Br_3$.

Oxidation of pongamol with potassium permanganate proceeded very smoothly and rapidly and about 30% yield of benzoic acid was obtained. Further the substance gave an orange red colour on reduction with magnesium and alcoholic hydrochloric acid; by the action of sodium amalgam and subsequent acidification with strong mineral acid a red colour which faded slowly was obtained. These results indicate that pongamol belongs to the flavone group of compounds. It has also been noticed that in the Wilson's boric acid test³ using a mixture of boric and citric acids in acetone solution, though there was no immediate formation of colour, a distinct yellow colour developed when the mixture was allowed to stand for about half an hour; this colour became more and more intense on further keeping. The significance of this observation is not very clear at present.

Degradation with alkali has again proved to be complex. Though pongamol does not dissolve easily in cold aqueous potash, it does so on warming and rapidly undergoes decomposition. Amongst the products obtained, the presence of benzoic acid is definitely established. The others are being studied.

Experimental

As has been described elsewhere,² pongamol was found to be present in the pongamia oil obtained by pressing or by solvent extraction and in the press-cake. However experience showed that the most convenient source for getting the compound in appreciable quantity was a stale sample of the expressed oil from which karanjin, together with free fatty acids, had been removed by a process of natural deposition. This oil (1 litre) was extracted with methylated spirit continuously in a special apparatus for about 40 hours. The solvent was distilled off from the extract as far as possible, when a yellow solid mixed with some oil was obtained. In case no solid separated as above the thick oily residue was allowed to stand for a few days; thereupon

big crystals usually separated from the oil. In either case the purification of the solid was effected by treating the magma with a little ether when the oily portion alone dissolved. After decanting off the ether solution and repeating the operation a few more times a pure solid melting at 123° was obtained (yield 1 gm.). Crystallisation of this from alcohol-acetic acid mixture gave pongamol as large pale yellow crystals (rhombic prisms) melting at 128–29°. A mixed melting point with karanjin (m.p. 158°) was considerably depressed (Found: C, 73.6, 73.5; H, 4.5, 5.0; OCH₃, 10.5; C₁₈H₁₄O₄ requires C, 73.5; H, 4.8; OCH₃, 10.5%).

The compound was insoluble in water, sparingly soluble in alcohol and moderately soluble in acetic acid. Aqueous sodium hydroxide did not dissolve it in the cold but decomposed it readily on boiling with the production of aromatic odour. Pongamol dissolved in concentrated sulphuric acid to give a yellow solution which turned deep emerald green in the course of five minutes. The fresh yellow solution in this acid also exhibited a green fluorescence which was rapidly lost. An alcoholic solution of pongamol gave an intense red colour with ferric chloride.

The molecular weight of pongamol was first determined by Rast's method using camphor as the solvent. But the result did not correspond to either of the formulæ C₉H₇O₂ or C₁₈H₁₄O₄. A value falling into line with the empirical formula and with the methoxyl content was, however, obtained by the cryoscopic and ebullioscopic methods using benzene as the solvent [Found: by Rast's method 220, by cryoscopic method 280, by ebullioscopic method 300. C₉H₇O₂ = 147; C₁₈H₁₄O₄ = 294; minimum molecular weight from methoxyl content (10.5%) = 295.]

Acetylation of pongamol was attempted using acetic anhydride and sodium acetate. After boiling for 5 hours the mixture was poured into excess of cold water and allowed to stand overnight. Only a liquid product was left behind which did not solidify even after prolonged standing in the refrigerator. It was easily soluble in methyl alcohol but no solid could be obtained from this solution by any means.

The methylation of pongamol using potassium carbonate and excess of methyl iodide in boiling acetone solution gave rise to a product which remained a viscous liquid even after repeated attempts to purify it by means of organic solvents. The benzylation was similarly carried out by treating pongamol with benzoyl chloride in boiling benzene solution. After distilling off most of the solvent and decomposing the excess of benzoyl chloride with water the mixture was ether extracted and the extract shaken with an aqueous solution of sodium bicarbonate to remove benzoic acid. The residue obtained by distilling off the solvent was also a viscous liquid which could not be

converted into the solid form by crystallisation from solvents. The use of pyridine in small quantities as a condensing agent or in larger quantities as a solvent did not make any difference.

A greater measure of success, however, attended the preparation of the *p*-nitrobenzoate which was accomplished as follows. The compound (0.5 gm.) dissolved in benzene (10 c.c.) was treated with *p*-nitrobenzoyl chloride (0.5 gm.) and the mixture was heated under reflux on a boiling water-bath for about 12 hours. The solution gradually acquired a dark green colour. It was then poured into an evaporating basin and left in a good draft of air to get rid off as much of the solvent as possible. The residue was treated with dilute aqueous sodium carbonate and the mixture repeatedly ether extracted. The filtered ethereal solution was shaken with dilute sodium hydroxide solution to remove any free nitrobenzoic acid and then evaporated. The sticky solid thus obtained was extracted with small portions of hot alcohol. The first extract which was very dark yielded a small quantity of crystalline solid mixed with resin; this was discarded. The subsequent extracts gave a purer sample which was crystallised from aqueous acetic acid. Though fairly crystalline in appearance the crystal form was indefinite and the solid did not possess a definite melting point. It was free from traces of the original compound since it did not give a ferric chloride colour. It was therefore macerated with aqueous sodium carbonate to remove any traces of nitrobenzoic acid and left overnight in contact with the alkali and then filtered and washed with water and finally crystallised from dilute acetic acid. The melting point, however, was still indefinite. The *p*-nitrobenzoate melted at 200–5° with sintering at about 105° and when it was examined under the microscope rectangular rods and needles could be seen along with some nodules. (Found: C, 66.6; H, 3.8; $C_{25}H_{17}O_7N$ requires C, 67.7; H, 3.8%). Experiments using pyridine as the condensing agent were unsuccessful.

Oxidation with alkaline permanganate.

The compound (1 gm.) was dissolved in 5% aqueous potassium hydroxide (50 c.c.) with warming and shaking for about half an hour. The solution was then treated with 4% potassium permanganate solution (100 c.c.), added slowly during two hours with continuous shaking. Much warmth was produced throughout the addition. After leaving overnight the mixture was treated with excess of sulphur dioxide when a clear solution was obtained. It was filtered off from a small quantity of resinous material with the help of a fluted filter and then concentrated under reduced pressure. When the residual liquid began to turn turbid, distillation was stopped. A fair amount of a white solid separated from the liquid overnight. The filtered solution was repeatedly ether-extracted and the combined ether extract

concentrated by distillation until a thick liquid was obtained. This liquid, however, rapidly deposited big colourless prismatic crystals which were carefully ladled off and freed from traces of adhering liquid by pressing on the porous tile. The crystals now melted at 118–19° and were found to be those of benzoic acid.

The liquid, from which the above crystals separated, slowly solidified in half an hour. This solid on crystallisation from hot water also yielded benzoic acid melting at 115°. The total yield of benzoic acid in this experiment was 0.3 gm.

Demethylation of pongamol.

Using hydriodic acid.—Finely powdered pongamol (0.5 gm.) was gently boiled with hydriodic acid (d. 1.7, 15 c.c.) for 5 hours. The mixture was then diluted with water (20 c.c.), when a dark solid separated from the deeply coloured solution. On passing sulphur dioxide the solution lost most of its colour but the dark solid was practically unaffected. After pouring out the aqueous solution the solid was extracted with hot pyridine and the decanted pyridine solution treated with a little water. The black sticky solid that separated was discarded. Further addition of water to the hot solution deposited some more of this substance. The final aqueous pyridine solution gave on cooling a mass of woolly needles melting at 119–20°. On repeated recrystallisation from alcohol in which it was easily soluble it was obtained as long colourless needles melting at 145–46°. It was free from methoxyl groups; still it did not dissolve in cold aqueous sodium hydroxide and was only slowly dissolved on warming, with the production of an aromatic smell due to decomposition. Alcoholic ferric chloride gave no colour. Sulphuric acid gave a very pale yellow solution devoid of fluorescence whereas an alcoholic solution exhibited a blue fluorescence. (Found: C, 72.1, 72.1; H, 4.8, 4.1; $C_{17}H_{12}O_4$ requires C = 72.9, H = 4.3%).

Using aluminium chloride.—The compound (0.3 gm.) dissolved in benzene (30 c.c.) was treated with freshly powdered anhydrous aluminium chloride (3 gm.) and the mixture was kept gently boiling under reflux on a water-bath for about 40 minutes. The benzene was then distilled off and the residue treated with hydrochloric acid (1:1). The residual solid was filtered, washed with dilute hydrochloric acid and then with water and crystallised twice from alcohol. A yellow powder (plates and needles under the microscope) melting at 224–5° was thus obtained. It contained no methoxyl, dissolved in cold alkali giving a deep yellow solution and gave a pale green ferric chloride colour. Concentrated sulphuric acid dissolved it to give a colourless solution with a blue fluorescence. (Found: C, 72.7; H, 4.7; $C_{17}H_{12}O_4$ requires C, 72.9; H, 4.3%).

Action of bromine.

Pongamol (0.3 gm.) was dissolved in glacial acetic acid (7 c.c.) and treated with a solution of bromine in the same solvent. The absorption of bromine was rapid in the beginning. Excess of the reagent was added and the mixture which had warmed up perceptibly was left well stoppered at the laboratory temperature for 5 hours with occasional shaking. It was then poured into a large excess of water (200 c.c.) when a light precipitate was immediately formed. The supernatant liquid which was highly coloured owing to the excess of bromine used, slowly became less and less coloured as the mixture was left exposed to the air. The white solid was filtered after some hours and washed with plenty of water. Recrystallisation from solvents was not feasible since on warming a paste was invariably produced. The dry sample sintered at about 70° and slowly decomposed above 125°. (Found in the air-dried specimen: C, 36.3; H, 2.5, Br, 51.4; $C_{18}H_{14}O_4Br_4$ requires C, 35.2; H, 2.3; Br, 52.1%). It gave no colour with alcoholic ferric chloride and in sulphuric acid it dissolved rather slowly to give a very pale yellow solution.

Action of boiling acetone on the above bromo compound.

The tetrabromo compound (0.5 g.) was suspended in acetone (10 c.c.) and heated on a warm water-bath under reflux. Most of the solid dissolved in the solvent to give a pale yellow solution by the time boiling commenced; the remaining solid also went into solution in the course of ten minutes giving rise to a clear orange red solution. After boiling for one hour the solvent was distilled off from the water-bath as far as possible. The last portions of the distillate as also the residue had a very irritating smell and were highly lachrymatory, obviously due to the formation of bromoacetone. The residual oil was freed from bromoacetone still remaining in it by boiling with water and decanting off the clear aqueous portion while hot. After a second repetition of the process the aqueous extract was no longer lachrymatory and the warm plastic mass hardened to a solid on cooling. On gentle rubbing with a glass rod this disintegrated to a yellow powder.

Purification of the solid thus obtained was attempted using alcohol as the solvent, but the alcoholic solution did not deposit any solid on cooling. Addition of a small amount of water caused the separation of an oil which did not solidify on keeping. Hence the mixture was largely diluted with water and after standing for some time the aqueous portion was decanted off. Repetition of this washing with excess of water a number of times finally gave rise to a solid yellow powder which was filtered off. The substance thus got sintered at 65°, melted at 83° and decomposed vigorously at 100°.

It was microcrystalline in appearance and gave a yellow solution with sulphuric acid. The pale yellow solution in alcohol gave a brown-red colour with ferric chloride. (Found: C, 40.9; H, 3.0; Br, 44.0; $C_{18}H_{13}O_4Br_3$ requires C, 40.5; H, 2.4; Br, 45.0%.)

Summary

Pongamol, which is the second important crystalline component of the pongamia oil, has the molecular formula $C_{18}H_{14}O_4$ and contains a methoxyl group. It has also a phenolic or enolic hydroxyl group. Demethylation with aluminium chloride yields nor-pongamol whereas treatment with hydriodic acid gives rise to a product which is probably isomeric but does not possess phenolic properties. Treatment with bromine produces a tetrabromo derivative which on boiling with acetone yields a tribromo compound. Oxidation with potassium permanganate or decomposition with alkali yields benzoic acid. From these properties and from colour reactions it is suggested that pongamol is a flavone derivative containing a hydroxyl, a methoxyl and an ethylene double bond.

REFERENCES

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