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ON THE CONSTITUTION OF THE TANNIN FROM INDIAN TERIPODS

By H. G. Biswas

From the pod cases of *Caesalpinia digyna* a tannin (m.p 200 - 12°) has been isolated (acetyl derivative, a colourless crystalline solid, m p. 206° - 208° decomp.). From the analytical data and study of hydrolysis the tannin has been proved to be a monodigalloyl glucose.

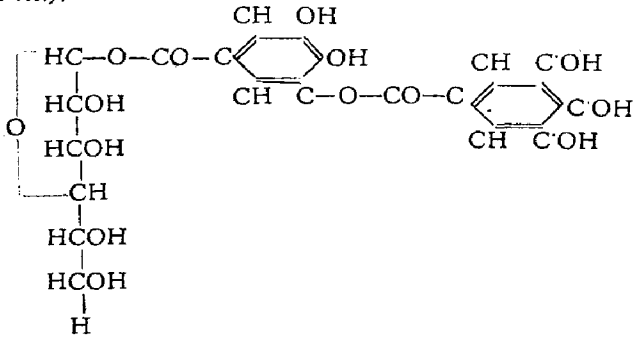
Caesalpinia digyna grows in the Eastern and Western peninsula, Assam, Bengal, Burma, Sambalpur, Ceylon and Eastern Himalayas. It is a large woody shrub. The pods are oblong, turgid, glabrous and 1½ - 2" in length, containing 2 to 4 pea-like seeds. The pod cases contain a tannin, very suitable for making writing ink.

Teripods are known to contain an appreciable amount of tannin (Kirtikar and Basu, "Indian Medicinal Plants", p. 466).

Nierenstein remarks ("The Natural Organic Tannis", 1934, p. 194) "According to Dekker, divi-divi-tannin is probably identical with algarobillitannin ; and this probably also applies to the tannin present in teri-pods (*Caesalpinia digyna*)".

The outer skin of the ripe pods contains a red colouring matter and when extracted with the usual solvents it comes along with the tannin and it becomes very difficult to remove it in subsequent operations. It has been found, however, that by careful scraping off of the skin of the ripe dry pods or by using dry unripe pods, the tannin can be obtained colourless. It has been found by the author that divi-divi-tannin is quite different from the teripod tannin. The tannin is hydrolysed according to the method of Fischer and Freudenberg (*Ber.*, 1912, 45, 915) and 65% gallic acid are obtained (calculated for monodigalloyl glucose it would be 70·2%). The reducing sugar has been proved to be glucose (25%, monodigalloyl glucose would yield 37·1% glucose). The small yield of sugar may be attributed to the partial decomposition of it by sulphuric acid during hydrolysis. The acetyl derivative (m.p. 206-208°) has been prepared with acetic anhydride and pyridine in the cold (Fischer and Bergmann, *Ber.*, 1918, 51, 1797).

The results of hydrolysis and the analytical data for the tannin as well as for its acetyl derivative are in fair agreement with monodigalloyl glucose. Hence teripod tannin should have the formula $C_6H_{11}O_5-O-COC_{13}H_9O_7$, and it may be structurally represented as follows from analogy to glucogallin (Fischer and Bergmann, *loc. cit.*).



EXPERIMENTAL

Isolation of the Tannin.—Dry ripe teripods, the reddish skin of which was carefully scraped off, were powdered, seeds removed and extracted with absolute alcohol in a Soxhlet. The alcohol was completely removed from the extract on a water-bath and the residue dissolved in water (charcoal). The aqueous solution was evaporated to dryness in vacuum, yield 40 g. (from 95 g. of powdered teripods). The crude tannin was dissolved in a little water, made slightly alkaline to litmus with sodium bicarbonate and then thoroughly extracted with ethyl acetate. The ethyl acetate extract was washed with water, dried over anhydrous sodium sulphate and the ethyl acetate was removed. The residue was again dissolved in a little water (charcoal) and the solution evaporated to dryness in *vacuo*. The colourless substance was powdered, dried in a steam bath and vacuum desiccator for several days. It melts with decomposition at 205-12°. It shows every characteristic reaction of tannic acid. (Found : C, 48·86 ; H, 4·58. $C_{20}H_{20}O_{14}$ requires C, 49·5 ; H 4·13 per cent).

Hydrolysis of the Tannin.—A solution of the tannin (5 g.) in sulphuric acid (5%., 250 c.c.) was heated on the water-bath for 30 hours. The solution on allowing to stand for a few days was treated with just sufficient quantity of baryta to remove H_2SO_4, the filtrate extracted several times with ethyl acetate till ferric chloride gave but a very faint colouration. The ethyl acetate extract was shaken with sodium chloride and then the solvent was completely removed. A brownish crystalline substance was obtained, yield 3·2 g. which crystallised from water, m.p. 224-26° (mixed m.p. with gallic acid). It gives pyrogallol on heating.

The sugar was isolated according to the method of Fischer and Freudenberg (*loc. cit.* 1912). To the mother-liquor obtained after removing gallic acid with ethyl acetate, lead carbonate (0·5 g.) was added, the solution boiled for 15 minutes, then in the hot, alternately a small amount of hot concentrated aqueous solution of monobasic lead acetate and lead carbonate added till it was neutral to litmus. CO_2 was passed through the solution till it was cold and filtered. The filtrate was warmed, H_2S passed into the solution and filtered. The filtrate was boiled to remove H_2S completely. The solution was concentrated in *vacuo* on a water-bath and left to stand for several days when crystals (1·2 g.) separated. It reduced Fehlings solution. A portion on recrystallisation melted at 140-42°. The osazone, prepared in the usual way, melted at 200°. The sugar is therefore glucose.

Acetylation.—Teripod tannin (1 g.) was gradually added to a mixture of 4 c. c. of acetic anhydride and 4 c.c. of dry pyridine ; during addition it became warm so it was cooled and then left to stand at room temperature for 3 days. On pouring into ice-cold dilute sulphuric acid an oil separated which solidified on keeping overnight. It was collected, washed with water and dried in a vacuum desiccator. It was then dissolved in 5 c.c. of dry chloroform and on pouring it into 50 c.c. of dry methyl alcohol, cooled in a freezing mixture, white crystalline precipitate appeared. It was quickly filtered and dried in a vacuum desiccator. The acetyl derivative is a microcrystalline colourless substance, m.p. 206-8° (decomp.). An acetone solution of it gave no

colouration with ferric chloride and it is insoluble in water. [Found : C, 55·0 ; H, 4·3. $C_{20}H_{11}O_{13}(CH_3CO)_9$ requires C, 55·5 ; H, 4·44 per cent].

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CONDENSATION OF 3 : 5-DINITRO-4-CHLOROBENZALDEHYDE WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES

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3 : 5-Dinitro-4-chlorobenzaldehyde (Mittal, *J. Indian Chem. Soc.*, 1942, **19**, 408) has been condensed with malonic acid using various organic bases and it has been found that the condensation takes place smoothly and the yield is almost quantitative when for one molecule of the aldehyde only one of the acid and 0·15—0·25 mol. of pyridine or a similar base are used, as has been previously observed in other cases (*cf.* Mittal, *J. Indian Chem. Soc.*, 1942, **19**, 47).

The condensations were carried out exactly following the method of Pandya (*J. Indian Chem. Soc.*, 1934, **11**, 824. *et seq.*).

Catalyst.	Amount of catalyst.	Yields	
Pyridine	0·15 mol.	1·09 g.	92·37 %
Piperidine	,,	1·05	88·98
Quinoline	,,	1·00	84·74
Without base	,,	0·59	50·00

This cinnamic acid was recrystallised from alcohol as yellow needles, m.p. 82°. (Found : N, 10·40 ; Cl, 12·85. $C_9H_5O_8N_2Cl$ requires N, 10·27 ; Cl, 13·02 per cent).

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