While all these ideas are bound to give new insights and may even go a long way towards the desired theory, in my opinion, they are unlikely to go all the way; as Bohr might have said, they are not "crazy enough". To be crazy enough, one must, I feel, abandon the use of space-time as the point of departure; space-time should emerge as a 'derived' concept, a macroscopic, averaged-out object. In this respect, two directions seem to be particularly promising. The first is provided by the notion of space-time foam; one begins with a microscopic model of space-time, consisting of a foam-like structure perpetually undergoing topological changes depicting quantum fluctuations. The second and more profound approach is the one involving spin-networks and twistors. Here, one takes the operational view that particles are more fundamental than space-time; space-time is recovered from spin-networks and twistor space which are themselves built directly from the momentum-angular momentum structure of particles.

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A NEW TANNIN FROM YOUNG STEM BARK OF *CAESALPINIA PULCHERRIMA*

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ABSTRACT

From the inner stem bark of three months old plants of *Caesalpinia pulcherrima* a new ellagitannin has been isolated which is unique in having a combination of condensed and hydrolysable tannin units in the molecule. Its structure has been established on the basis of analytical, degradative and spectroscopic evidences.

CAESALPINIA PULCHERRIMA[1] (subfamily: Caesalpinaceae, family : Leguminosae) known in Hindi as 'Guletrura' is a garden variety. In our earlier publications[2-5] we have reported the presence of *β*-sitosterol, sebacic acid, quercimeritrin, leucodelphinidin and two ellagitannins (A) and (B) from the stem bark. This bark is highly astringent and the astringency goes on decreasing with the age of the plant. We have studied the bark at different stages of growth in order to assess the chemical changes taking place specially in the polyphenols. In our earlier publication the bark of full-grown plants was studied. We now report the components of the younger bark.

The fresh inner stem bark of three months old plants of *C. pulcherrima* was extracted with alcohol free acetone. The concentrated extract was fractionated into petrol, ether and ethyl acetate soluble fractions. Petrol removed chlorophyll and *β*-sitosterol. Ether extracted gallic acid, sebacic acid and quercimeritrin; and ethyl acetate extracted mainly leucodelphinidin

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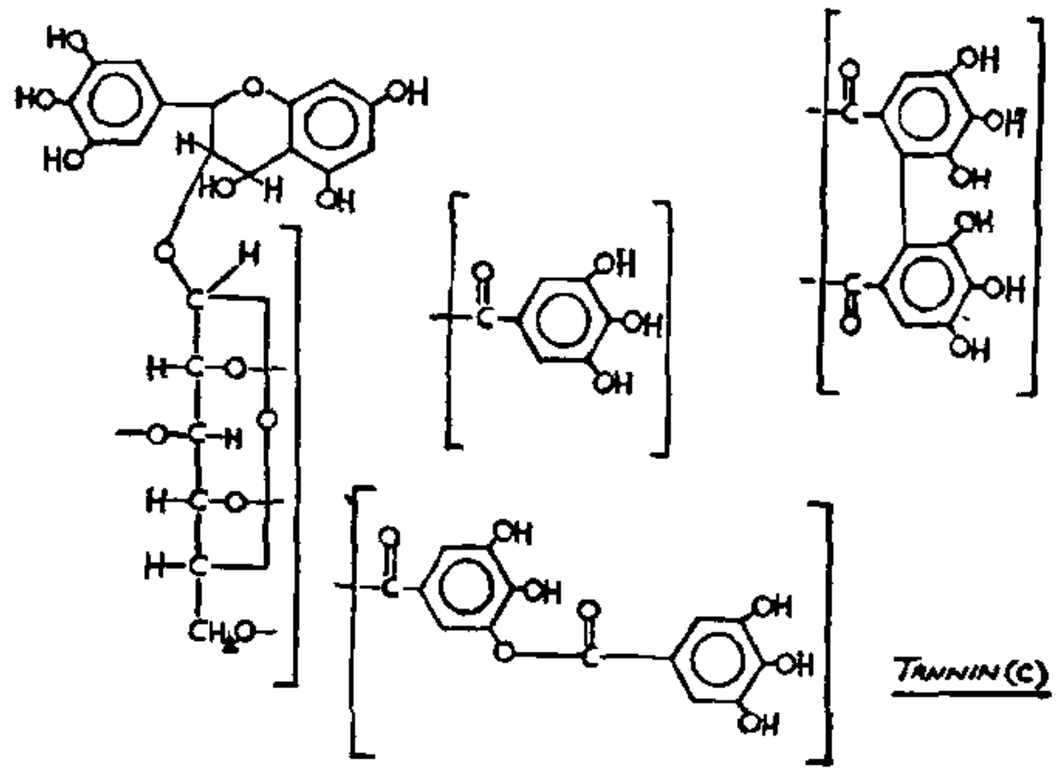
along with a very small amount of quercimeritrin. The remaining amorphous powder, on repeated maceration with acetone and subsequent purification by preparative TLC yielded a cream coloured homogeneous amorphous powder. This was marked as tannin (C).

Tannin (C)

Tannin (C), m.p. 258° (d) gave positive Molisch's test but negative test with aniline hydrogen phathalate[6], thereby indicating its glycosidic nature. Acid hydrolysis gave gallic acid, ellagic acid, glucose and anthrocyanidin identified as delphinidin by its $\lambda_{max}^{ETOH-HCl}$ 557 nm (lit : 560 nm) and mixed paper chromatography with an authentic sample isolated from solanum melongena fruit coat hydrolysate[7]. On alkali hydrolysis, gallic acid, ellagic acid and a resinous mass was obtained from the hydrolysate which could not be characterised. The acetyl estimation of the tannin acetate ($COCH_3$: 41·36%) indicated the presence of twenty hydroxyl groups in the tannin molecule. The diazomethane methylated tannin on alkali hydrolysis gave 3, 4, 5 tri-O-methylgallic, 3, 4-di-*o*-methyl gallic and 3, 4, 5, 3′, 4′, 5′ hexamethoxydiphenic acids in the ratio 2 : 1 : 1. These acids were identified by comparisons with the prepared synthetic samples. Hexamethoxydiphenic acid was prepared by a new procedure by subjecting 2-iodo-3, 4, 5-tri-O-methylgallic acid to Ullmann reaction[8] using copper bronze. The relative proportions of the three acids were ascertained by comparative PC using prepared mixtures of the acids in different ratios for references. The presence of the dimethylgallic acid indicated the presence of depside links in the tannin, *i.e.*, a polygalloylated chain. As no *m*-tri digallic acids could be detected during methanolysis of the tannin, the possibility of a polygalloylated chain was completely excluded. The distribution of galloyl, *m*-digalloyl and hexahydroxydiphenoyl units on the glucose core is of course, random.

In addition to the three acids, a colourless crystalline glycoside could be isolated from the alkali hydrolysate of the tannin methyl ether, which on acid hydrolysis gave glucose and pentamethyldelphinidin λ_{max}^{ETOH} 530 nm, chromatographically identical with a prepared sample of the same. It could therefore be concluded that leucodelphinidin molecule may be attached to C–1 of glucose glycosidically through either 3 or 4 OH of its diol unit. This could be decided by subjecting this glycoside to catalytic hydrogenation when no free sugar could be detected in the solution, thereby suggesting the glycosidic linkage at position 3, (linkage with benzylic 4–OH should have been cleaved). The complete hydrolysis of this glycoside with almond emulsin proved the stereochemical nature of the glycosidic linkage as β. Tannin (C) is a novel type of ellagitannin incorporating in its structure both condensed as well as hydrolysable tannin molecule. Such a nucleus has not so far been reported in nature, although such a combination is feasible biogenetically. With the growth of the plant the hydrolysis of the glycoside linkage setting the leucodelphinidin molecule and the reducing group of the carbohydrate core free while the ester linkages are kept intact, is interesting from the biogenetic point of view.

The presence of this tannin (C) in good yield (0·12%) in the bark of young plants probably accounts for its high astringency which decreases later, as with the growth of the plant the glycoside linkage is metabolides.



TANNIN (C)

EXPERIMENTAL

Plant material

The stem bark of young *C pulcherzima* plants was collected locally from Allahabad.

Solvents used for chromatography

(i) PC : Solvent a_1 : *n*-BuOH-HOAc-H_2O (4 : 1 : 5) solvent b_1 : *n*-BuOH saturated with NH_3 and solvent c_1 : Moist PhOH (1 : 9).
(ii) TLC : Solvent a_2 : C_6H_6-Me_2CO (6 : 4).
(iii) PLC : Solvent b_2 : C_6H_6-MeOH (2 : 8).

Isolation of tannin (C)

The fresh inner stem bark (0·5 kg.) was extracted with EtOH free Me_2CO (3 × 0·5 l) at room temp. The combined Me_2CO extract (1·5 l) conc. under red. pres. The dark greenish brown viscous conc. was macerated with petrol, Et_2O and EtOAc respectively. Petrol extract contained traces of chlorophyll and β-sitosterol, Et_2O extract was found to contain free gallic acid along with segacic acid and quercimeritrin in traces and EtOAc yielded leucodelphinidin along with very small amount of quercimeritrin. These were identified by mmp, co-chromatography with authentic samples. Further maceration with Me_2CO

and subsequent purification from Me_2CO-Et_2O followed by PLC (solvent : b_2) gave an amorphous compound m.p. 258° (d), (Found : C, 54–15: H, 3·2 $C_{56}H_{42}O_{33}$ requires : C, 54·10; H, 3·38%). It gave dark blue ppt. with EtOH-$FeCl_3$ and red colour on boiling with 10% EtOH-HCl. It gave positive Molisch's test but did not give any significant colour when sprayed with aniline hydrogen phthalate reagent on paper followed by heating at 100°. It gave single spot on PC with R_f 0·26 (solvent : a_1; spray : EtOH $FeCl_3$) and also on TLC (solvent : a_2). UV λ_{max} 280 mm, IR γ_{max}^{KBr} : 3350 (OH), 2910, 1730 (depside), 1600 (aromatic), 1530, 1440, 1370, 1320, 1190 and 1040 cm^{-1}.

Acetate

The tannin (0·03 g) refluxed with Ac_2O (5 ml) and NaOAC (0·05 g) at 140° for 4 hr. The acetate was obtained as colourless solid m.p. 266° (d). (Found : C, 55·56; H, 3 96; $COCH_3$, 42·55: $C_{96}H_{82}O_{53}$ requires : C, 55·33; H, 3·93; $COCH_3$, 41·30%).

Acid hydrolysis

The tannin (0·1 g) was refluxed with EtOH-H_2SO_4 (25 ml, 7%) for 2 hr. A cream coloured solid separated out. The solution was cooled and filtered, solid was identified as ellagic acid by Griessmayer test[9] and mixed chromatography with the synthetic sample prepared by the method of Perkin and Nierenstein[10], and finally by its UV λ_{max} 255 nm and IR γ_{max}^{KBr} : 3550, 1620, 1740, 1720, 1520, 1430, 1360, 1100, 1060, and 920 cm^{-1}. IR was superimposable on that of synthetic sample.

The solution was extracted with Et_2O which showed the presence of an acid identified as gallic acid. The remaining solution was then extracted with amyl alcohol, which extracted all the colour and responded to colour tests similar to naturally occurring anthocyanidin. The anthocyanidin was identified as delhpinidin by its $\lambda_{max}^{EtOH\text{-}HCl}$ 557 nm (lit. 560 nm) and mixed chromatography with an authentics ample of delphinidin obtained from the *Solanum melongino* fruit coat hydrolysate[7]. The remaining solution on neutralisation and concentration gave syrupy residue which responded to tests for glucose, confirmed by Co-PC, R_f 0·18 (solvent : a_1 : spray; aniline hydrogen phthalate) with an authentic sample of glucose.

Acid hydrolysis (quantitative)

The tannin (0·1 g) dissolved in EtOH-H_2SO_4 (15 ml, 7%) was refluxed for 2 hr. The solution was cooled to room temperature and solid separated was centrifuged and washed with H_2O dried at 100° and weighed. After removing ellagic acid the remaining solution was extracted with Et_2O. The Et_2O solution was concentration and the residue dissolved in H_2O and made upto 100 ml. It was subjected to potentiometric titration against 0·1 solution of KOH. The remaining solution was neutralised with $BaCO_3$, $BaSO_4$ filtered and washed with H_2O. The filtrate and washings were combined and made upto 50 ml. The sugar was estimated by Folin's and Wu's calorimetric method (Found : ellagic acid 24·30%; gallic acid 41·2%; glucose 14·3%; $C_{56}H_{42}O_{33}$ requires ellagic acid 24·31%; gallic acid 41·06% and glucose 14·49% respectively).

Alkali hydrolysis

The tannin (0·1 g) dissolved in EtOH-NaOH (5 ml, 10%) was kept at room temp. for 24 hr. out of contact with air. It was then acidified with glacial HOAc and continuously extracted with Et_2O. The Et_2O extract on PC gave R_f 0·75 and 0·36 (solvent : a_1; spray : EtOH-$FeCl_3$) corresponding to gallic acid (R_f 0·74) and ellagic acid (R_f 0·35). The aq. solution on concentration gave a brown resinous mass which could not be characterised.

Methylation and hydrolysis

On methylation with CH_2N_2 the tannin (0·2 g) gave a white solid which crystallised from Me_2CO-Et_2O mixture as colourless crystals, m.p. 260° (d). The tannin methyl ether (0·2 g) was taken in EtOH 15 ml, NaOH (10 ml, 5%) added and the mixture was kept for 48 hr at room temperature out of the contact with air. The solution was extracted exhaustively with Et_2O. The Et_2O extract gave three spots on PC (solvent : b_1; spray : bromophenol blue) R_f 0·59, 0·38 and 0·14 corresponding to 3:4 dimethylgallic acid, trimethylgallic acid and hexamethoxydiphenic acid. The area and intensity of the spots suggested the presence of these acids in 1 : 2 : 1 proportion. It was further ascertained by comparative PC using artificial mixtures of these acids prepared from the authentic samples of 3 : 4 dimethylgallic acid, trimethylgallic acid and hexamethoxydiphenic acid in different prportion, *viz.*, 1 : 1 : 1, 1 : 2 : 1, 1 : 3 : 1, 2 : 3 : 1, 2 : 3 : 2 etc. The trimethylgallic acid[11] was prepared by wet methylation of gallic acid using Me_2SO_4 and aq. NaOH, the dimethylgallic acid by controlled methylation of gallic acid using calculated amount of Me_2SO_4 and refluxing in Me_2CO-K_2CO_3 for 4 hr. Hexamethoxydiphenic acid was prepared by Ullmann reaction[8] of 2-iodo-3, 4, 5-tri-*o*-methylgallic acid prepared by iodination of tri-*o*-methylgallic acid.

Alkali hydrolysis: pentamethyl leucodelphinidin glucoside

The CH_2N_2 methylated tannin was hydrolysed with NaOH (10 ml, 5%) and kept for 48 hr. at room temp. and the solution extracted with Et_2O. The residual solution gave positive Molisch's test but neither reduced Fehlings solution nor gave any positive colour with aniline hydrogen phthalate reagent. This

solution was continuously extracted with EtOAc. The combined EtOAc extract was concentration and excess of petrol added when a colourless compound was obtained, which crystallised from EtOAc-petrol as small prisms. It did not give any characteristic, colour with EtOH-$FeCl_3$ solution. The compound (0·01 g) was boiled with EtOH-HCl (10 ml, 15%) for 30 min when it gave an anthocyanidin which did not give any colour with $FeCl_3$, $\lambda_{max}^{EtOH-Hcl}$ 530 nm.

Catalytic hydrogenation

The pentamethyl leucodelphidin leucoside (0 02 g) obtained above was dissolved in EtOH (40 ml) and platnium oxide (0·05 g) was added. The hydrogenation was carried out at atm. pres. for 4 hr. The resulting solution was, distilled to remove excess of EtOH. The concentration solution neither reduced Fehlings solution nor gave positive colour test with aniline hydrogen phthalate reagent. Similar results were obtained when 15 atm. pres. was applied.

Methanolysis

The tannin (0·05 g) was dissolved in 0·5 N acetate buffer (5 ml; pH 6·0) and to it MeOH (25 ml) was added. The solution was kept at 35° for 7 days. The MeOH was then removed by distillation under red pres. The residue was continuously extracted rith EtOAc. The EtOAc extract on PC gave two spots R_f 0·74 and 0·82 (solvent : a_1; spray; EtOH–$FeCl_3$) corresponding with gallic acid (R_f 0·75) and methylgallate (R_f 0·83).

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DOMINANCE HIERARCHY AND DIVISION OF LABOUR IN THE SOCIAL WASP, *ROPALIDIA MARGINATA* (LEP.) (HYMENOPTERA : VESPIDAE)

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ABSTRACT

The presence of a dominance hierarchy among the workers of a *Ropalidia marginata* colony can be recognized on the basis of pair-wise interactions. This hierarchy influences the division of labour on the colony in a manner such that the subordinate individuals spend more time making trips to places away from the nest to bring back food, building material, water etc. while the dominant ones like the queen, sit around and at best give alarm reactions. This is consistent with the result that it is the heavier individuals that develop their ovaries and are capable of becoming egg layers.

INTRODUCTION

IT is a well established fact that dominance hierarchies are an important component of social life in animals (Schein[7], Kramer *et al.*[2]). However, there have been relatively few studies of dominance hierarchies in the social insects. The few reports that do exist are primarily concerned with dominance among foundresses on pre-emergence colonies or dominance of workers over subordinate foundresses (Pardi[6]; West-Eberhard[10]; Hermann and Dirks[5]; Spradbery[8]; West[9]; Wilson[11]). In this paper I report the presence