Table 1 *Dielectric data for different solute molecules in dilute solution in benzene.*

Molecule	Dielectric parameters				Relaxation time in p. seconds				Dipole moments in Debye units			
	a_0	a'	a''	a_∞	$\tau(1)$	$\tau(2)$	τ_{GK}	τ_{GG}	μ_H	μ_{GK}	μ_{GG}	μ_{GU}
Propionaldehyde	11.62	11.11	1.90	0.37 (4.03)†	3.1	4.7	2.6	2.2	3.02	2.23	3.00	2.14
Acrolein	14.80	12.50	2.78	0.40 —	4.0	14.3	8.2	3.9	3.42	2.67	2.70	2.54
Crotonaldehyde (in CCl_4)	13.16	10.59	5.00	0.21 (0.86)	8.3	10.4	7.8	7.2	3.24	2.77	3.15	2.70
Furfural	15.00	10.00	5.31	0.09 (4.36)	9.3	16.3	12.0	8.7	3.48	3.36	3.59	3.68
Cinnamaldehyde	12.00	4.71	2.96	0.34 (3.51)	11.7	42.5	13.0	12.1	3.08	2.71	2.96	3.58
Vanillin	6.91	2.93	2.00	0.44 (1.93)	13.9	34.5	5.9	21.6	2.29	2.25	2.49	2.63
P-Tolualdehyde	6.25	4.00	3.25	0.12 —	14.47	11.96	12.5	13.8	2.23	2.78	2.84	3.06

† The values in the paranthesis in this column correspond to the values of $(a_\infty)_{cal}$ as calculated by equating $\tau(1) = \tau(2)$.

under consideration are characterised by more than one Debye type dispersion. Similar conclusions are arrived at in some other substituted anilines in dilute solution systems[9]. However, it may be mentioned that in the case of dilute solution systems it is hard to visualise the multiple relaxation processes but actual measurements at another higher frequency may be a more useful guide to decide this factor than the random difference criterion only.

Further details regarding the behaviour of τ values and electric dipole moments of these molecules may be found in literature[10, 11].

The authors are thankful to Dr M. I. Savadatti, for encouragement.

1. Dakin, T. W. and Works, C. N., *J. Appl. Phys.*, 1947, **18**, 789.
2. Gopalakrishna, K. V., *Trans. Far. Soc.*, 1957, **53**, 767.
3. Guggenheium, E. A., *Trans. Far. Soc.*, 1949, **45**, 714; 1951, **47**, 573.
4. Keniti Higasi, Yoshinori Koga and Masatiko Nakamura, *Bull. Chem. Soc., Jpn*, 1971, **44**, 988.
5. Keniti Higasi, *Bull. Chem. Soc., Jpn*, 1966, **39**, 2157.
6. Vij, J. J. and Srivastava, T. K., *Trans. Far. Soc.*, 1970, **66**, 1087.
7. Ghosh, A. K. and Ghosh, S. K., *Indian J. Pure Appl. Phys.*, 1982, **20**, 743.
8. Kazuo Chitoku and Keniti Higasi, *Bull. Chem. Soc., Jpn*, 1971, **44**, 993.
9. Amarsingh, Saxena, S. K. and Saxena, M. C., *Indian J. Pure Appl. Phys.*, 1982, **20**, 276.
10. Deshpande, D. K. and Suryanarayana Rao, K. Dr Bhagavantam's Commemoration Volume, 1969, 33.
11. Deshpande, D. K. and Suryanarayana Rao, K., *Curr. Sci.*, 1966, **35**, 360.

15 September 1983

A NEW TANNIN FROM *ACACIA LEUCOPHLOEA* STEM BARK

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THE highly astringent bark of *Acacia leucophloea* has been reported to contain varying amounts of tannins. In the present communication we report the isolation and characterisation of isookanin, cyanin, leucodel-

phinin and a new tannin which has been assigned a probable structure based on chemical and spectroscopic studies.

The air-dried and powdered stem bark was extracted with acetone under reflux extract, concentrated and fractionated into light petrol, ether, ethyl acetate and acetone soluble fractions. Light petrol fraction on chromatography confirmed the findings of Joshi *et al*[1]. Ether fraction was found to contain one flavonoid compound identified as isookanin and ethyl acetate fraction contained traces of cyanin and leucoanthocyanin characterised as leucodelphinidin-3-O-α-L-rhamnopyranoside. From the acetone soluble fraction a new tannin was isolated.

Isookanin[2], cyanin[3], leucodelphinidin-3-O-α-L-rhamnopyranoside[4] were identified by comparing with the respective authentic samples.

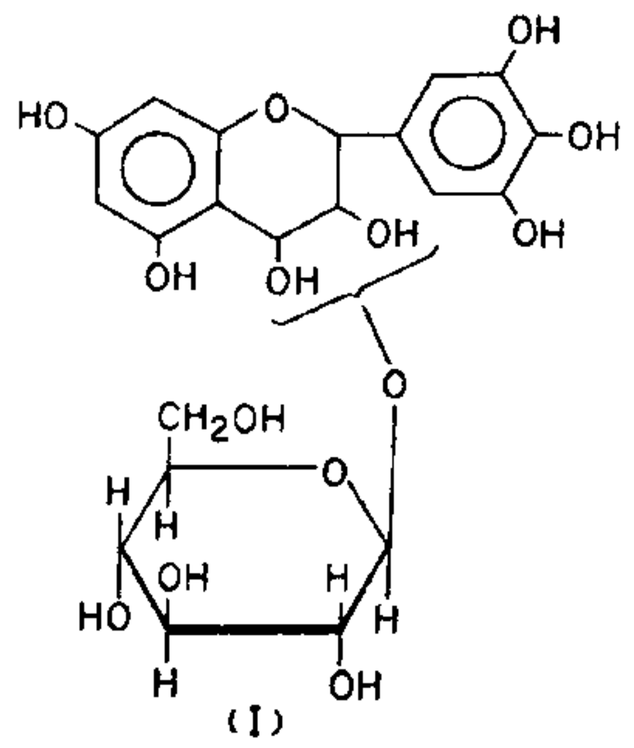
The tannin was a chromatographically homogeneous, amorphous compound, m.p. 237°(d). λ_{max}^{MeOH}: 278 nm. IR: 1710 cm^{-1} (notched, characteristic for ester and depside linkages). It gave positive Molisch test and blue black precipitate with ferric chloride[5], and negative test with aniline hydrogen phthalate reagent suggesting it to be a polyphenolic reducing glycoside. On acid hydrolysis with 7% alcoholic sulphuric acid, it gave an anthocyanidin, a phenolic acid along with glucose. The anthocyanidin extracted with amyl alcohol from the hydrolysate, could be identified as delphinidin by its colour tests. $\lambda_{max}^{EtOH-HCl}$: 557 nm (lit. 560 nm)[6] and direct comparison with an authentic sample extracted from *Solanum melongena* fruits[7]. Subsequent extraction of the hydrolysate with ether gave gallic acid and glucose was identified in the remaining solution by paper chromatography and osazone formation.

The glycoside could be hydrolysed with alkali yielding gallic acid and indicating ester linkages. Therefore, the compound could be a galloylated glucose derivative. Quantitative acid hydrolysis of tannin followed by estimation of glucose by Folin and Wu's method[8], and gallic acid by potentiometric titration showed glucose (14.47%) and gallic acid (61.08%) calculating to five moles of gallic acid per mole of glucose.

Isolation of delphinidin from the acid hydrolysate of this compound showed the presence of prodelphinidin unit which must be linked through glycosidic linkage at anomeric carbon of glucose.

The tannin on methylation with diazomethane afforded a methyl ether $C_{56}H_{25}O_{14}(OCH_3)_{19}$ and the tannin acetate analysed for $C_{56}H_{25}O_{14}(COCH_3)_{20}$. The methyl ether on alkali hydrolysis gave 3,4-di-O-methyl gallic acid and 3,4,5-tri-O-methyl gallic acid along with an ethyl acetate soluble glycoside. This glycoside on acid hydrolysis gave glucose and delphinidin pentamethyl ether. Therefore, in the glycoside the glucose C-1 is linked to leucodelphinidin moiety at position 3 or 4 of the diol group through a C–O–C linkage as indicated by its easy hydrolysis. Periodate oxidation of the methylated glycoside and consumption of 2 moles of periodate with liberation of one mole of formic acid, confirmed pyranose structure of glucose.

The hydrolysis of the glycoside linkage with emulsin[9,10] confirmed its stereochemical nature as β. Therefore, structure (I) was suggested for the glycoside.



(I)

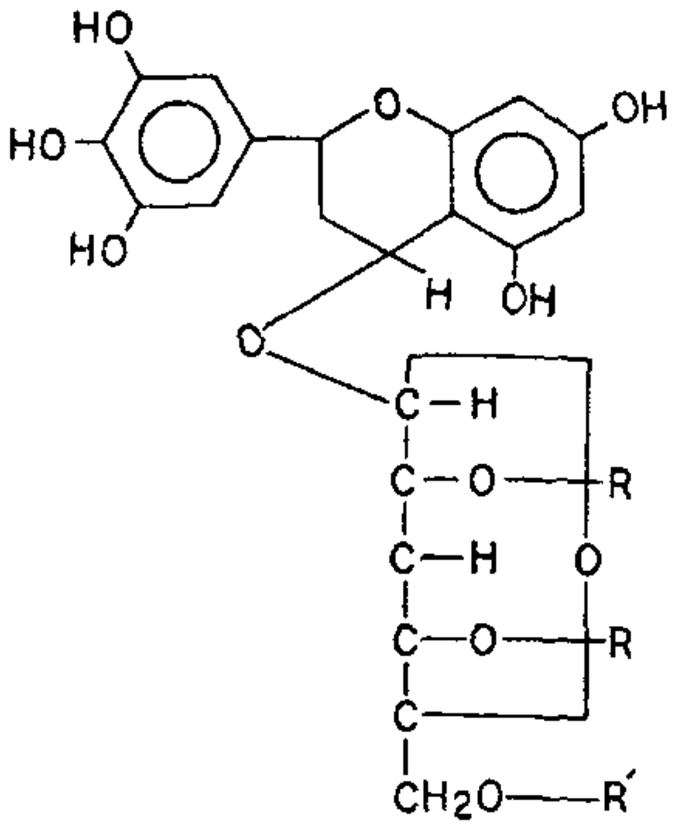
The ratio of 3:4:5-tri-O-methyl and 3:4-di-O-methyl gallic acids was ascertained by comparative paper chromatography as 4:1 respectively. The isolation of 3:4-di-O-methyl gallic acid in the hydrolysate indicated the presence of depside linkage in the molecule.

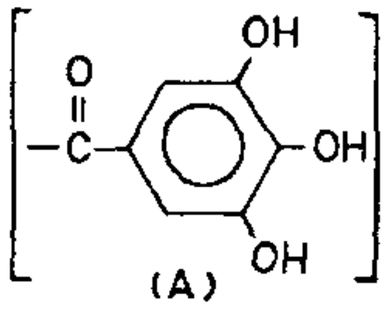
The extent of depside linkages between gallic acid units was ascertained by subejecting the tannin to methanolysis, which gave methyl gallate along with an artefact tannin (IIA) but no *m*-digallate or tri-gallic acids were detected in the resulting solution.

The artefact tannin (IIA) on acid hydrolysis gave glucose and gallic acid along with delphinidin. The tannin on quantitative hydrolysis gave 55.32% gallic acid thereby suggesting the presence of four gallic acid units per mole of glucose.

As C-1 of glucose is involved in glycosidic linkage with leucodelphinidin molecule and glucose is present in pyranose form, the remaining sugar hydroxyls at C-2, C-3, C-4 and C-5 must be involved in galloylation.

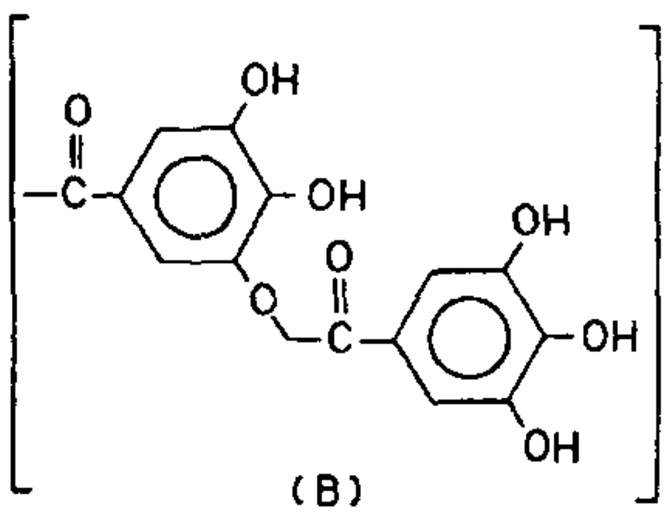
No *m*-digallic or tri-gallic acid could be detected during methanolysis; therefore, the probability of the





(A)

II (A) R = R′ = A
(B) R = A, R′ = B



(B)

presence of trigalloyl or tetragalloyl chain was excluded. It was, therefore, obvious that only one *m*-digalloyl unit is present in the molecule. The exact position of the *m*-digalloyl unit on glucose core, could not be decided, distribution of three galloyl and one *m*-digalloyl units being random. A tentative structure (IIB) could be assigned to the tannin, based on the fact that in majority of the naturally occurring gallotannins the polygalloylated chain is consistently present at C-6, primary hydroxyl of glucose. This position is also sterically favourable. Spectral data (UV, IR) also confirm the assigned structure.

30 March 1983; Revised 17 December 1983

1. Joshi, K. C. and Sharma, T., *J. Indian Chem. Soc.*, 1977, **54**, 649.
2. Clark-Lewis, J. W. and Porter, L. J., *Aust. J. Chem.*, 1972, **25**, 1943.
3. Willstatter, R. and Bolton, E. K., *Ann.* 1916, 412, 136.
4. Shukla, R., Trivedi, K. K. and Misra, K., *Planta Med. Suppl.*, 1980, p. 48.
5. Briggs, L. H. and Locker, R. H., *J. Chem. Soc.*, 1951, 3136.
6. Jurd, L., In: *The chemistry of flavonoid compounds*, (ed.) Geissman, Pergamon Press, Oxford, 1962, p. 132.
7. Kuroda, C. and Wada, M., *Proc. Imp. Acad. (Tokyo)*, 1935, **11**, 237.
8. Folín and Wu, *J. Biol. Chem.*, 1929, **82**, 83.
9. Richter, D., *J. Chem. Soc.*, 1936, 170.
10. Peat, S., Whelan, W. J. and Hinson, K. A., *Nature (London)*, 1952, **170**, 1056.

STUDIES ON RING OPENING OF COUMARINS

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VARIOUS substituted O-methoxy cinnamic acids have been prepared by ring opening of coumarins using sodium hydride and methyl iodide in dry tetrahydrofuran[1]. The use of sodium hydride-methyl iodide combination was justified by stating that alkaline hydrolysis of coumarins in the presence of dimethyl sulphate yielded predominantly trans-O-methoxy cinnamic acids[2]. However, a careful analysis of the report[2] reveals that *cis*-isomer was obtained exclusively and not a mixture with trans-predominance as understood by Sehgal *et al*[1]. In view of this misrepresentation in the literature, it was considered worthwhile to reinvestigate this reaction with particular emphasis on the examination of the effect of changing the methylating agent from methyl iodide to dimethyl sulphate and also to understand the role of sodium hydride in the ring opening of coumarins.

The starting material could only be recovered when the reaction was carried out under identical conditions[1]. In view of this inability to reproduce the results, the reaction was carried out under various experimental conditions. The observations are summarised in table 1.

It is seen from table 1 that no change could however be effected by the use of sodium hydride dispersed in oil or pure sodium hydride or aqueous sodium hydroxide. The reaction could not also be effected in an inert atmosphere. Substituted *cis*-O-methoxy methyl cinnamates were however obtained when the reaction was carried out at room temperature with many-fold excess of methyl iodide. Hence an alternate methylating agent, namely dimethyl sulphate, was employed with a