

[Be(H₂O)₄]. Hence further dissociation of BeF₄ into BeF₃+2F⁻ and of BeF₂ into Be⁺⁺ and 2F⁻ in a solution of fluoroberyllic acid is not possible.

The average value for K₁ was found to be 3.46×10⁻³ and the mean deviation being 0.7×10⁻³. The large variation in the values from the average may be attributed to the overlapping dissociation⁵ which takes place when the first and second dissociation constants do not differ by more than 10³.

2. *Cryoscopy*.—Cryoscopic experiment was carried out with water as the solvent. The acid did not affect glass at high dilution.

The following results were obtained :

Room temperature	.. 26° C,
Strength of fluoroberyllic acid	.. 2.55%
Mean ΔT _f for 2.55% fluoroberyllic acid	= 1.61°
Apparent Mol wt.	= 29.47
Degree of dissociation	= 0.9765
Dissociation constant	= 2.37×10 ⁻³

The average value of three determinations of the first dissociation constant of fluoroberyllic acid was in fair agreement with that obtained by the potentiometric method.

Ionic Mobility of Fluoroberyllate Ion

The ionic mobility of fluoroberyllate ion was obtained from the conductance of the sodium, potassium and ammonium salts of the acid.

The equivalent conductances of sodium and potassium salts of the acid were determined with paraffin coated conductivity cell at different concentrations and extrapolated to infinite dilution.

Substance used	Equiv. cond. at infinite dilution Ohm ⁻¹	Ionic cond. of cations ⁵ Ohm ⁻¹	Ionic cond. of BeF ⁻² Ohm ⁻¹	Ionic mobility of BeF ₄ ⁻²
Sodium fluoroberyllate	112	43.3	68.60	7.1×10 ⁻⁴
Potassium fluoroberyllate	133.2	64.6	68.60	7.1×10 ⁻⁴
Ammonium fluoroberyllate	134.1	64.3	68.60	7.2×10 ⁻⁴

Solubilities of Difficultly Soluble Salts of Fluoroberyllic Acid

The specific conductances of the saturated solutions were calculated, after deducting the value for pure water.

Results

Solubilities of fluoroberyllates of	S×10 ⁻³
Calcium 1.67
Barium 1.25
Strontium 1.43
Lead 1.88

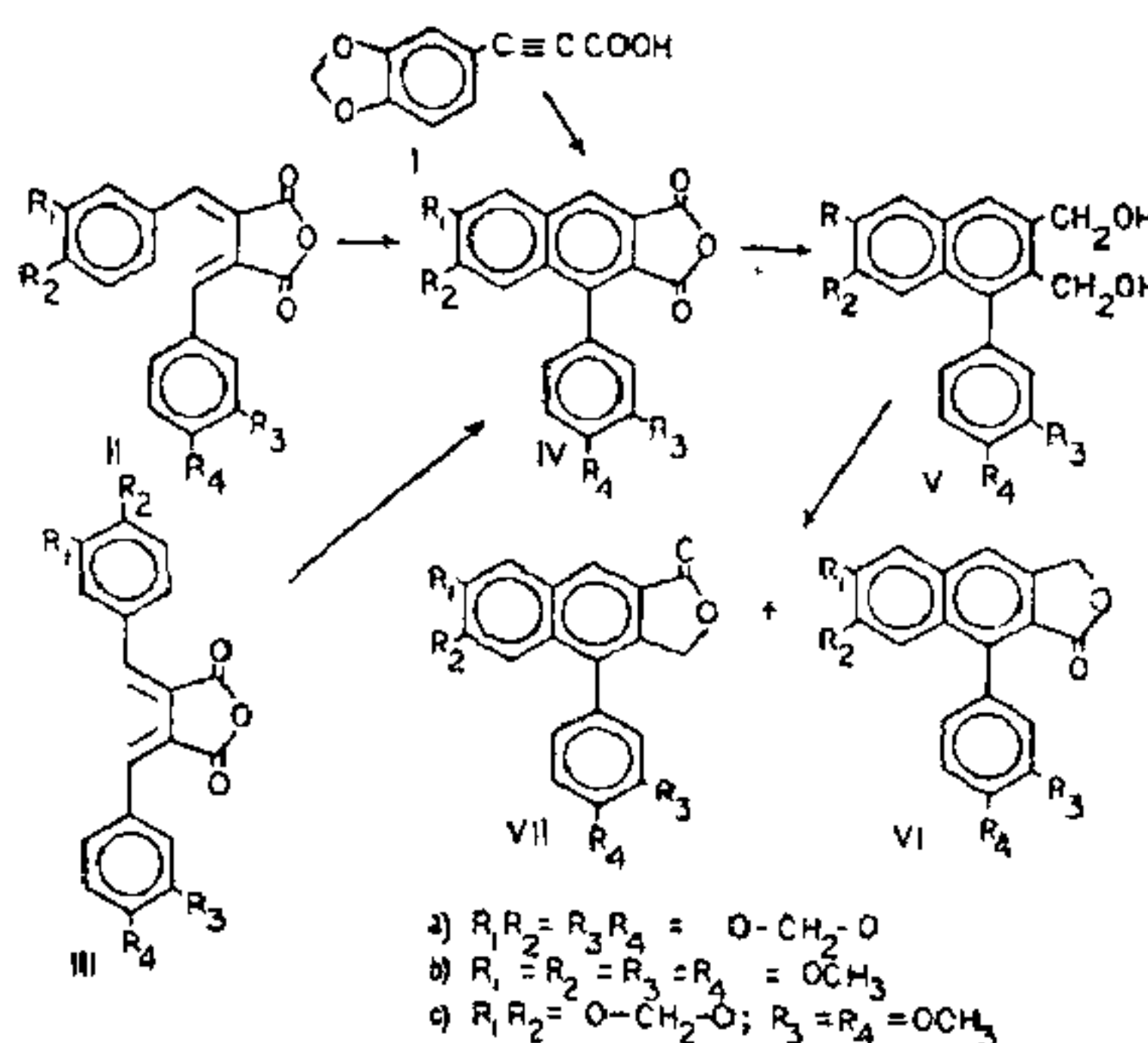
Author's grateful thanks are due to Dr. N. N. Ray formerly Reader in Chemistry, University College of Science, Calcutta, for his guidance and interest in the work, and to Dr. T. N. Chakravarty for his help.

Inorganic Chemistry Lab., TARUN K. GHOSH.
University College of Science,
Calcutta, February 2, 1974.

1. Ray, N., *Z. anorg. allg. Chem.*, 1939, 241, 165.
2. Ghosh, T. K., Chakravarty, T. N. and Ray, N., *J. Ind. Chem. Soc.*, 1965, 42, 847.
3. Boral, A. K., Saha, H. K. and Ray, N., *J. Inorg. Nucl. Chem.*, 1967, 29, 2490.
4. Mee, A. J., *Physical Chemistry*, William, Hanemann Ltd. Publication.
5. Glasstone, S., *Introduction to Electrochemistry*, D. Van Nostrand Publication.

A NEW SYNTHESIS OF JUSTICIDIN E AND TAIWANIN C

RECENTLY, Holmes and Stevenson¹ reported the synthesis of justicidin E (VII a)² and taiwanin C (VI a)³ from 1-piperonyl propiolic acid (I). A facile alternate synthesis of these lignins is now reported starting from *trans, trans*-dipiperonylidene-succinic anhydride (III a).



The successful use of Pb(OAc)₄-AcOH to cyclise diarylidenesuccinic anhydrides was recently reported 'from these laboratories'⁴. But, this reagent had no effect on *trans, trans*-dipiperonylidene-succinic anhydride (III a) under varying conditions. The *cis, trans*-isomer (II a), which accompanied the former (III a) as a minor product in its synthesis⁵, cyclised in 5 hrs and the yield of 1-piperonyl naphthoic anhydride (IV a) was 50%. After several trials, it was observed that addition of a trace of HClO₄ to the reaction mixture caused the ring closure of III a in 1.5 hrs to give IV a in 60%. Under similar conditions, cyclisation of the isomer (II a) was complete in 1 hr and the yield of IV a was 80%.

6,7-methylenedioxy-1-(3',4'-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic acid anhydride (IV a) crystallised as yellow needles, m.p. 222–225° from acetone⁵ and m.p. 240–242° from chloroform-methanol⁶. IR(CHCl₃): 1845 and 1780 cm⁻¹ (anhydride); Found: C, 66.28; H, 3.0; C₂₀H₁₀O₇ requires C, 66.31 and H, 2.78%.

The use of HClO₄ resulted in effecting the ring closure of the resistant *trans, trans*-isomer, and also improved the yields and reduced the reaction times considerably. It was next extended to the cyclisation of symmetrical diveratrylidenesuccinic anhydrides (II b and III b) and also to the unsymmetrical

colourless needles, m.p. 270–272° (lit.¹ 271–272°), IR (CHCl₃): 1755 cm⁻¹ (lactone) and was identical (mmp & IR) with an authentic sample of justicidin E, kindly gifted by Dr. Stevenson. The isomeric lactone (IV a, yield 16%) crystallised from benzene as colourless prisms, m.p. 275–276° (lit.¹ 272–276.5°), IR (CHCl₃): 1760 cm⁻¹ (lactone) and agreed in all its physical characteristics recorded in literature^{1,3} for taiwanin C.

The two naphthoic anhydrides (IV b and IV c) were also similarly converted into the corresponding pairs of lactones, through the diols V b and V c (Table I).

TABLE I

Naphthoic anhydride	Diol	Lactones	
		A	B
IV b	V b	VI b	VII b
m.p. 310–312° (lit. ¹ 305–306°)	m.p. 189–190° (lit. ¹ 189–190°)	m.p. 253–255° (lit. ¹ 253–255°)	m.p. 216–217° (lit. ¹ 215–216°)
IV c	V c	VI c	VII c
m.p. 270–271° (lit. ⁴ 270°)	m.p. 180–182° (lit. ⁴ 179–180°)	m.p. 229–230°	m.p. 240–242°

veratrylidene, piperonylidenesuccinic anhydride (II c). In the former case, the mixture of II b and III b from Stobbe condensation was not separated, but warmed with Pb(OAc)₄-HOAc and a trace of HClO₄. The cyclisation was complete in 15 mts and the yield of IV b⁴ was 90%.

In the case of the unsymmetrical veratrylidene, piperonylidenesuccinic anhydride, only the *cis, trans*-isomer (III c)⁴ was formed in the Stobbe condensation and it cyclised in 1.5 hrs to give 80% of the naphthoic anhydride IV c⁴. It may be pointed out here that the course of cyclisation of III c was not altered by the use of HClO₄ and the naphthoic anhydride was identical with that obtained earlier⁴.

The conversion of IV a to justicidin E and taiwanin C was next effected following the method adopted by Holmes and Stevenson¹. Reduction of the naphthoic anhydride (IV a) to the diol (V a) was accomplished by LAH in THF at reflux temperature and the diol (V a) crystallised from benzene, m.p. 188–189°, IR(CHCl₃): 3400 cm⁻¹. It was then refluxed with silica gel-Ag₂CO₃ instead of celite-Ag₂CO₃ (cf. Ref. 1) in benzene solution for 2 hrs and the resulting isomeric lactones (VI a and VII a) were separated by column chromatography over silica gel using benzene as eluent. The lactone (VII a, yield 30%) crystallised from benzene as

The structure of the lactones (VI c and VII c) were assigned from a study of their ¹H NMR spectra in which significant difference in the chemical shifts can be expected for the lactone methylene protons. The compound with m.p. 229–230° (IR, 1750 cm⁻¹ for the lactone; Found: C, 69.60; H, 4.38; C₂₁H₁₆O₆ requires C, 69.23 and H, 4.43%) is assigned the structure VI c, for the lactone methylene protons appeared as a singlet at δ 5.31 as in taiwanin C (IV a)¹. In the isomeric lactone, m.p. 240–242°, (IR, 1755 cm⁻¹ for lactone, Found: C, 69.03; H, 4.61; C₂₁H₁₆O₆ requires C, 69.23 and H, 4.43%), the lactone methylene protons appeared high field at δ 5.13 s as in justicidin E (VII a)¹ and therefore it is represented by the alternate structure VII c.

Two of us (V. K. R. and A. M. R.) wish to express our grateful thanks to CSIR, New Delhi, for the Fellowships. Our thanks are also due to Professor N. V. Subba Rao, Osmania University, Hyderabad, for the NMR spectra.

Department of Chemistry, A. S. R. ANJANEYULU,
Andhra University, V. KAMESWARA RAO,
Waltair 530003, A. MADHUSUDHANA RAO,
February 27, 1974, I. RAMACHANDRA RAO.

Note added in proof:

We came across a recent publication (B. J. Arnold, S. M. Mellows and P. G. Sammes, *J. Chem.*

Soc., Perkins I. 1973, p. 1256) in which a new synthesis of the title compounds was reported by a longer and arduous route (about 12 stages).

1. Holmes, T. L. and Robert Stevenson, *J. Org. Chem.*, 1971, 36, 3450.
2. Lin, Y. T., Io, T. B., Wang, K. T. and Weinstein, B., *Tet. Letters*, 1967, p. 849.
3. Wada, K. and Munakata, K., *Ibid.*, 1970, p. 2017.
4. Anjaneyulu, A. S. R., Kameswara Rao, V., Satyanarayana, P. and Ramachandra Row, L., *Ind. J. Chem.*, 1973, 11, 203.
5. Chakraborty, D. P., Thomas Sleigh, Robert Stevenson, Gertrude A. Swoboda and Boris Weinstein, *J. Org. Chem.*, 1966, 31, 3342.
6. Holmes, T. L. and Robert Stevenson, *J. Chem. Soc. (C)*, 1971, p. 2091.

ANTHOCYANIN OF SUGARCANE

IN an earlier note¹ it was mentioned that the peelings of sugarcane contain two flavone glycosides. We now report the isolation of an anthocyanin from this plant.

The reddish brown peelings of sugarcane were extracted with ethanolic hydrochloric acid at room temperature. The concentrate was kept in the cold and the residue thus obtained crystallised from alcohol-HCl mixture as chocolate coloured crystals. It gave positive Molisch test and other reactions characteristic of anthocyanins.

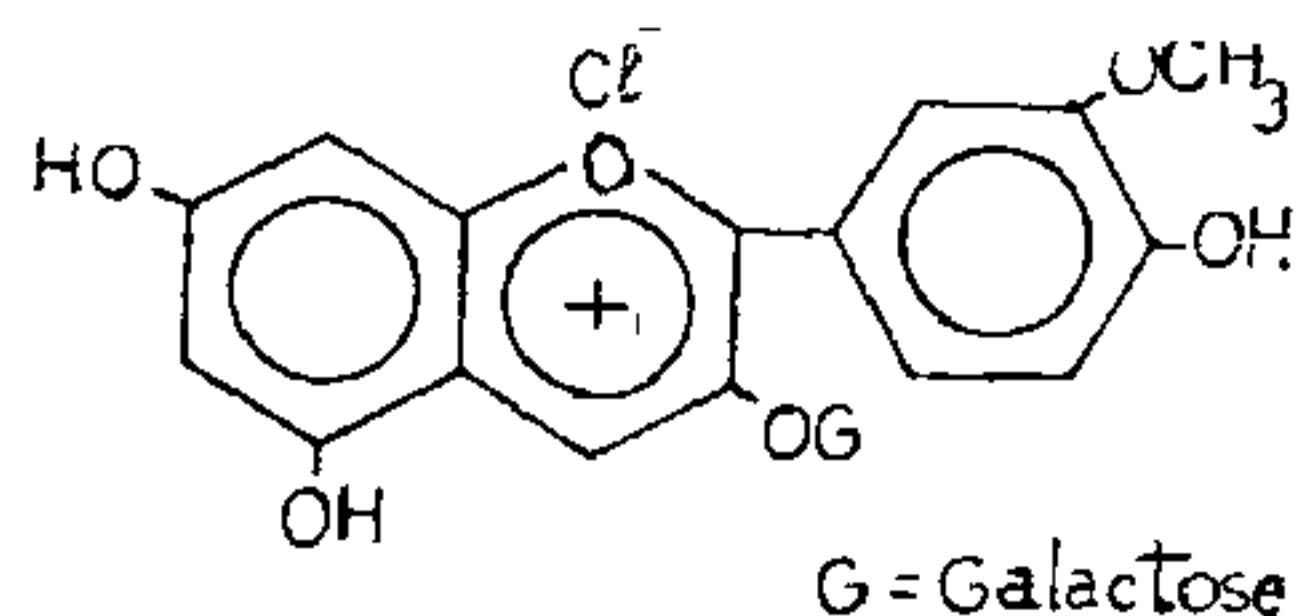
The glycoside on hydrolysis with 20% HCl yielded an anthocyanidin, which could be precipitated with petroleum ether from amyl alcohol solution into 1% aqueous HCl layer. It crystallised as dark reddish brown prisms from ethanolic-hydrochloric acid mixture.

From the hydrolysate, a sugar was isolated which was identified as D (-) galactose by its osazone and co-chromatography with an authentic sample. Quantitative sugar estimation showed it to be a mono-galactoside.

Various colour tests indicated that the anthocyanin or its aglycone did not contain free vicinal hydroxyl groups in the attached benzene ring. Quantitative estimation by Ziesel method confirmed the presence of one methoxyl group. The anthocyanidin and anthocyanin both gave specific colour reactions of peonidin derivatives and had λ_{\max} at 542 and 532 m μ respectively in ethanolic solution. A hypsochromic shift of 10 m μ in the glycoside² was an indication of the probable position of sugar at 3. The peonidin structure was further supported by no shift in the λ_{\max} for either glycoside or aglycone with 1% AlCl₃ reagent.

Oxidation of anthocyanidin with KMnO₄ yielded vanillic acid and its alkali fission gave phloroglucinol,

both identified by co-chromatography on paper and mixed m.p. with authentic samples. Finally the anthocyanidin was confirmed as peonidin by co-chromatography on paper using Forrestal solvent with an authentic sample of peonidin isolated from fresh viola tricolor flowers. Hence the structure (I) has been assigned to the anthocyanin from sugarcane.



(I)

It is for the first time that peonidin-3-mono-galactoside is being reported in this plant, although the presence of delphinidin, indicated only by colour tests, has been reported earlier in this source³.

We convey our thanks to Prof. R. D. Tewari for his interest in the present work and also to SCSIR (U.P.) for the grant of assistantship to R. C. D.

Department of Chemistry,
Allahabad University,
Allahabad, June 18, 1974.

(Mrs.) K. MISRA,
R. C. DUBEY.

1. Dubey, R. C. and Misra, K., *J. Ind. Chem. Soc.* (in press).
2. Jurd, L., *The Chemistry of Flavanoid Compounds*, (Ed.) Geissman, T. A., Pergamon Press, 1962, p. 134.
3. Rao, C. J. D., *J. Ind. Chem. Soc.*, 1938, 15, 27; Rao, M. N., *Ind. Sugar*, 1941, 4 (3), 28; Tinbergen-Van, J. C., *Der Vloedt. Chem. Weekblad*, 1937, 34, 254; Sakuma, I. and Momose, I., *J. Soc. Chem. Ind. Japan*, 1935, 38, 224 and 293.

ISOLATION OF 3, 3', 4-TRI-O-METHYL- FLAVELLAGIC ACID FROM BARK OF *ANOGEISSUS LATIFOLIA*

Anogeissus latifolia is a large and moderate sized tanniferous tree¹ and earlier workers² isolated ellagic acid (I) and 3, 3', 4-tri-O-methyl-ellagic acid (II) from the bark. By continuous soxhlet extraction of the powdered bark with chloroform, it has now been possible to isolate a yellow compound, m.p. 280-1° (dioxane); M⁺ 360, C₁₇H₁₂O₉; $\nu_{\max}^{\text{nujol}}$ 1685 (>C=O), 1705 (>C=O), 3280 (-OH) cm⁻¹; $\lambda_{\max}^{\text{EtOH}}$, 245 (4.60), 366 (4.00), 382 (4.04) nm. These absorptions are highly charac-