

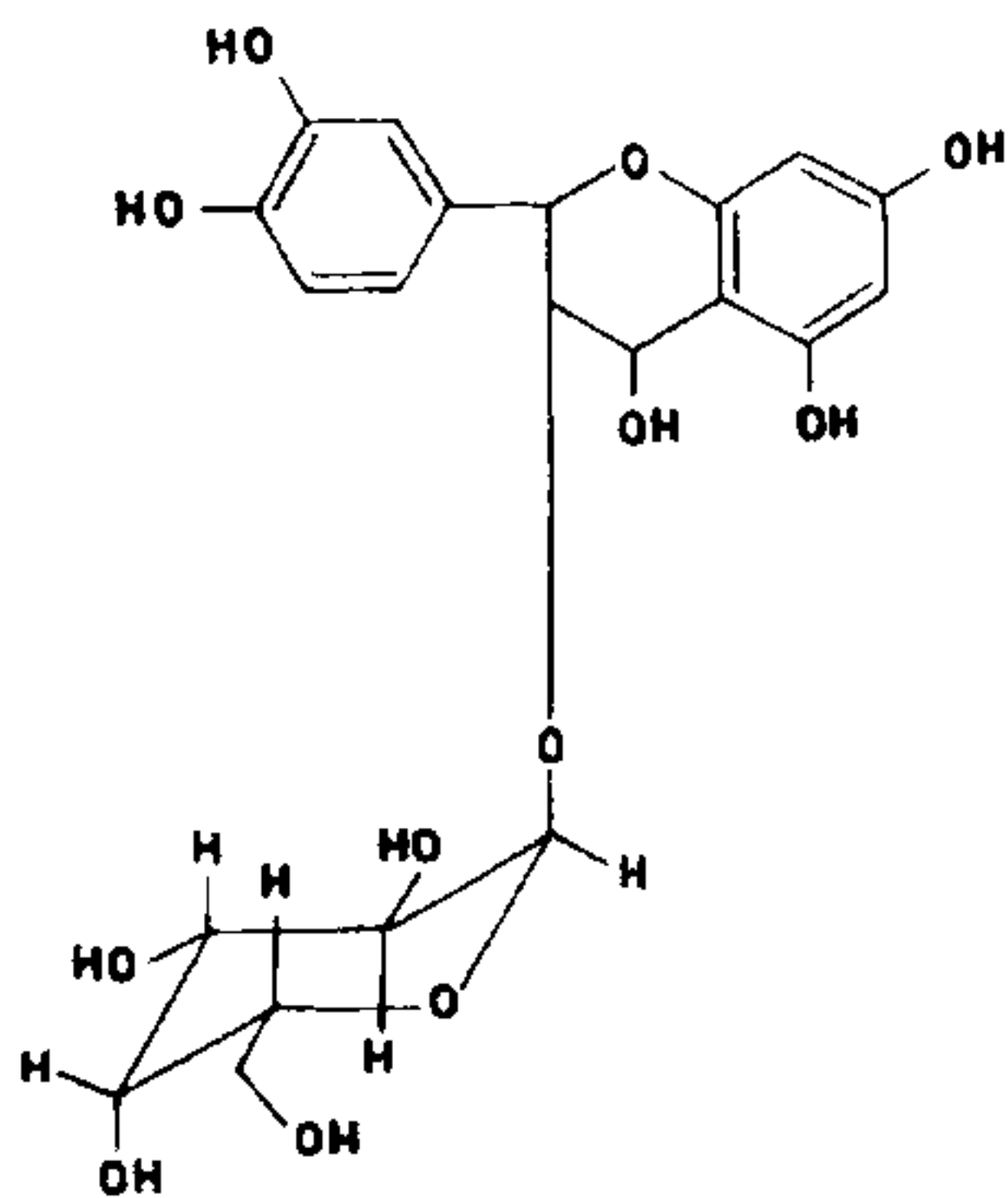
SHORT COMMUNICATIONS

A NEW LEUCOANTHOCYANIN FROM
PELTOPHORUM FERRUGINIUM BARKNEETA KHARE*, REKHA GUPTA
and P. C. GUPTADepartment of Chemistry, University of Allahabad,
Allahabad 211002, India.

A NEW Leucoanthocyanin isolated from the stem-bark of *Peltophorum ferruginium* (N. O. Leguminosae) has been characterized as Leucocyanidin 3-O- α -D-galactopyranoside on the basis of spectral data, colour reactions, and degradation studies.

*Peltophorum ferruginium*¹ is reputed for its medicinal importance. From the seeds of this plant, auxins² have already been reported.

From the ethyl acetate extract of the stem bark, a new glycoside has been isolated. Its homogeneity and purity were established by paper and thin layer chromatography.

Leucocyanidin-3-O- α -D-galactopyranoside

The compound was analyzed as $C_{21}H_{24}O_{12}$, m.p. $186^\circ(d)$, R_f 0.23 (TLC BuOH-AcOH- H_2O : 4:1:5 v/v), $[\lambda]_{max}^{EtOH}$ 284 nm. It gave positive Molisch's test and negative test with aniline hydrogen phthalate reagent³ indicating it to be glycosidic in nature. The glycoside gave different shades of colour with EtOH/HCl, EtOH/ $FeCl_3$, Ammonium molybdate/acetic acid, ammonia and vanillin-HCl indicating the glycoside to be

Leucoanthocyanin. On hydrolysis with 10% ethanolic-HCl, the glycoside gave D-galactose (m.p. 164° , $[\alpha]_D^{30} + 80^\circ$ (water); D-galactose phenyl hydrazone m.p. 153°)⁴ and an anthocyanidin identified as cyanidin (colour reactions, paper chromatography, $[\lambda]_{max}^{EtOH-HCl}$ 544 nm, $[\lambda]_{max}^{EtOH-AlCl_3}$ 560 nm and comparison with an authentic sample of cyanidin isolated from fresh rose petals⁵). This indicated the glycoside to be Leucocyanidin galactoside.

The acetate of Leucoanthocyanin m.p. 119° , analyzed as $C_{21}H_{15}O_{12} (COCH_3)_9$ and its methyl ether (with only phenolic hydroxyls methylated), m.p. 104° analyzed as $C_{21}H_{20}O_8 (OCH_3)_4$, suggesting the presence of four phenolic and five alcoholic hydroxyls⁶ in the molecule.

On permethylation⁷ and subsequent hydrolysis, the glycoside yielded 2,3,4,6-tetra-O-methyl-D-galactose (identified by Co-p.c., m.p. $72-73^\circ$, $[\alpha]_D^{33} + 120^\circ$ and R_{TMG} (0.87) values)⁸. The methylated glycoside on acid hydrolysis gave an anthocyanidin $[\lambda]_{max}^{EtOH-HCl}$ 524 nm corresponding to tetra methyl cyanidin. The hypsochromic shift of 20 nm suggested the substitution of all the free phenolic hydroxyls. Thus it could be concluded that sugar is not linked at positions C_5 , C_7 , C_3 , or C_4 . The only alternative left is the 3-4 diol group.

Prolonged acid treatment of the glycoside yielded a polymeric substance whereas the completely methylated glycoside lacked this property indicating the presence of free benzylic hydroxyl⁹ at C_4 . Therefore the C_3 hydroxyl must be involved in the glycosidic linkage. This was further confirmed by subjecting the glycoside to catalytic hydrogenation (Pt/H_2)¹⁰ when no free sugar could be detected. Had the sugar been linked at benzylic C-4 hydroxyl the glycosidic linkage should have been cleaved. The suggested biogenesis of these compounds¹¹ also favours position-3 for glycosidic linkage. Easy hydrolysis of the glycoside with the enzyme taka-diaxase indicate it to be an O-glycoside, and the sugar linkage as $-\alpha$ (IR. ν_{max}^{KBr} 822 cm^{-1}).

Quantitative periodate oxidation¹² of the tetra-methyl glycoside (with only phenolic hydroxyl methylated) yielded 1.02 mol of formic acid with the consumption of 1.98 mol of sodium metaperiodate per mole of the methylated glycoside. This proved that galactose is present as a monosaccharide and in the pyranose form (supported by a peak at 822 cm^{-1} in the IR spectrum)¹³.

The Leucoanthocyanin could therefore be designated as Leucocyanidin 3-O- α -D-galactopyranoside.

The suggested structure was in conformity with its IR and NMR data.

IR: $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3320 (OH group), 1620, 1500, 1470 (aromatic ring), 1260, 1150, 1040 (w) and 822 (sugar moiety).

NMR: (CDCl_3 , 60 MHz); (values in τ): 6.5 (m, 6-H, sugar protons), 5.80 (m, 1H, 3-H), 5.00 (m, 1H, 2-H), 4.70 (m, 1H, 4-H), 4.3 (m, H-1, galactosyl), 3.88 and 3.80 (each d, 2H, 6- and 8-H), ($J_{6,8}$ 2.3 C/S), 2.80 (d, 2H, 2'- and 6'-H).

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EVALUATION OF EXCESS INTERNAL PRESSURE IN BINARY LIQUID MIXTURES OF WATER WITH ASSOCIATED LIQUIDS

A. P. SRIVASTAVA and S. N. TRIPATHI
Chemical Laboratories, K. S. Saket (P. G.) College,
Faizabad 224001, India.

INTERNAL pressure has been used as an important parameter¹⁻⁸ to study the inter-molecular interactions between binary liquid mixtures. Pandey *et al*⁹ showed that excess internal pressure, like other thermodynamic properties varies with change in composition and temperature of the systems.

Recently excess internal pressure has been evaluated in binary liquid mixtures containing nonassociated liquids viz *n*-hexane + dichloromethane, *n*-hexane + 1,2-dichloroethane and *n*-heptane + dichloromethane, and *n*-heptane + 1,2-dichloroethane. The study has been extended to correlate this excess property with intermolecular interactions¹⁰. In the present investigation the associated organic liquid has been taken and the excess internal pressure has been evaluated in the binary liquid mixtures of water + *t*-butanol, water + *n*-propanol, water + ethylene glycol, and water + glycerol at 25°C. The ultrasonic velocity and density data have been taken from literature¹¹.

Theory:

The internal pressure was evaluated by the following equations:

$$P_i V \left(1 - \frac{d}{a}\right) = RT, \quad (1)$$

$$v = a^3 / \sqrt{2}, \quad (2)$$

$$P_i = \frac{2^{1/6} RT}{(2^{1/6} V - d N^{1/3} V^{2/3})}, \quad (3)$$

$$d^{5/2} = \frac{1}{7.21 \times 10^{19}} \cdot \frac{V r^{1/4}}{T_c^{1/4}}, \quad (4)$$

$$T_{c_m} = \sum_{i=1}^2 X_i T_{c_i}, \quad (5)$$

$$r = 6.30 \times \rho \times U^{3/2} \times 10^{-4}. \quad (6)$$

All the symbols in (1) to (6) have the usual significance described elsewhere¹⁰.

The excess internal pressure is given by

$$P_i^E = P_{i(m)} - \sum_{i=1}^2 X_i (P_i)_{id}. \quad (7)$$