the central interaction just based on the spin orders.

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ACTION OF PERIODATE ON FLAVANDIOLS

THE use of periodic acid as a glycol-splitting agent is well known.[1] This has been made use of in the structural studies of flavan-3, 4-diols. Earlier oxidation studies have been carried out with naturally occurring leucoanthocyanidins. The periodic acid consumption of leucocyanidin has been quantitatively estimated.[2] It consumes 2 moles accounting for the glycol and catechol units. However, for the isolation of the oxidation products the methylethers are more convenient. King and Bottomley[3] isolated 2-hydroxy, 3, 4-dimethoxy benzaldehyde as its semicarbazone by the oxidation of melacacidin methyl ether with periodic acid. Veratraldehyde and phloroglucinaldehyde dimethyl ether were isolated[4] when leucocyanidin methyl ether was treated with an aqueous solution of periodic acid (50%) for 24 hr. at room temperature. The following mechanism has been suggested.

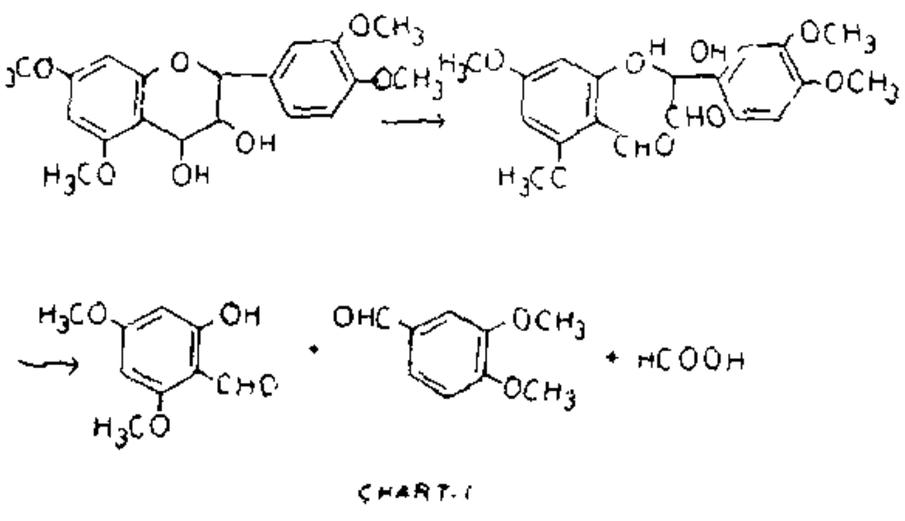


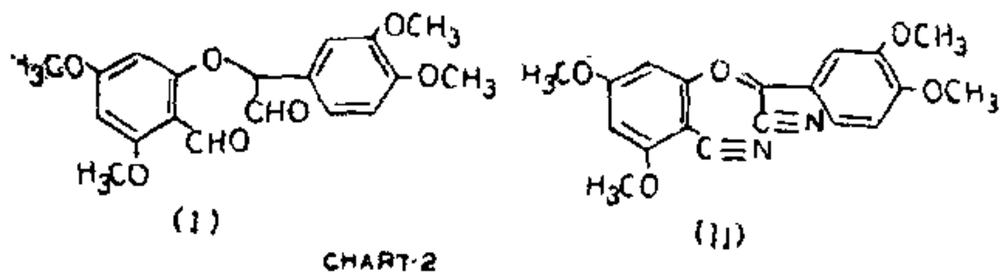
CHART-I

More recently periodic acid has been used in determining the configurations of leucoanthocyanidins.[5] When the methyl ethers are employed, the *cis* diol consumes 1 mole of periodic acid in about 7 min. whereas the *trans* is much slower and takes 40 minutes.

There has been so far no definite criterion for the determination of the molecular size of leucoanthocyanidins as monomer, dimer, trimer or polymer. The method of using solubility in different solvents like ethylacetate has limited application and is not definite. On the basis that the 4-hydroxyl is involved in linking up with another polyphenol molecule and is thus locked up, it is possible to assay the end group by periodic acid titration. This is feasible only when the end group is a diol. If other polyphenols like catechins are involved then there will be no consumption of periodic acid. The method has quantitative application only in the case of homogeneous polymers. For determination of the constitution of new leucoanthocyanidin the fission method will be useful if both parts of the molecule could be obtained as recognisable units.

For purposes of standardisation of conditions and understanding the products, a leucoanthocyanidin of known structure was necessary. Therefore the synthetic leucocyanidin methyl ether has now been studied. It has been prepared by the borohydride reduction of taxifolin-5, 7, 3', 4'-tetra-O-methyl ether. Quantitative estimations using an aqueous solution of sodium metaperiodate (pH 6·4) showed that one mole of the synthetic sample consumes 1·1 mole of sodium metaperiodate. Under identical conditions glucose consumes 5·3 moles of periodate. Since the formation of veratraldehyde and phloroglucinaldehyde dimethylether needs the consumption of 2 moles of periodate, it can be concluded that the oxidation with an aqueous solution of sodium metaperiodate stops at the first stage, *i.e.*, with the formation of a dialdehyde. The product is definitely different from veratraldehyde or phloroglucinaldehyde dimethylether. The new aldehyde has been isolated as its oxime since the preparation of a 2, 4-dinitrophenylhydrazone would involve objectionably high acid concentrations. The mass spectrum of the oxime has been studied. The molecular ion peak of the oxime could not be obtained though the spectrum had peaks up to 368. The presence of peaks beyond 200 obviously rules out the simpler aldehydes mentioned above. Significant among the mass peaks is the peak at 353 which can be attributed to M-($2H_2O$.+ H) (II). Nitrogen estimation of the oxime shows it to be a

dioxime. Hence Structure I could be assigned to the aldehyde.



(I) (II)

CHART-2

EXPERIMENTAL

An aqueous solution of sodium metaperiodate (20 ml.; 2·503 g./250 ml.) is added separately to each of the following in aldehyde-free ethanol (30 ml.): (*a*) leucocyanidin methyl ether (0·025 g.), (*b*) analar glucose (0·025 g.) and distilled water (3 ml.), and (*c*) blank. After keeping the solutions for 48 hours a standard solution of arsenious oxide is added to each with shaking and allowed to stand for half an hour, excess of arsenious oxide was determined iodimetrically. From the amount of arsenious oxide the amount of periodate consumed has been calculated and given below:

Compound	Glucose	Blank	Leucocyanidin methyl ether
Moles of Periodate consumed	5·3	Nil	1·1

Isolation of the dioxime.—An aqueous solution of sodium metaperiodate (50 ml.; 2·503 g./250 ml.) is added to a solution of leucocyanidin methyl ether (0·1 g.) in aldehyde-free ethanol (100 ml.). After keeping the homogeneous solution for 48 hours, it was diluted and extracted repeatedly with ethyl acetate. The ethyl acetate extract was thoroughly washed with a saturated solution of bicarbonate and finally with water and dried over anhydrous magnesium sulphate. Removal of the solvent gave a semi-solid residue. It was taken up in alcohol and treated with hydroxylamine hydrochloride in presence of sodium acetate. The oxime crystallised from ethanol as colourless rods, m.p. 214–16° (Found N_2, 8·2%; $C_{19}H_{22}O_7N_2$ requires N_2, 7·2%).

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STUDIES ON THE USE OF BRUCIQUINONE AS A NEW ACID-BASE INDICATOR

BRUCIQUINONE, the red oxidation product of brucine, shows a pink colour in acid solutions and a yellow in alkaline solutions.

Our investigations have shown that this substance serves as a good acid-base indicator. The results obtained are reported below:

Bruciquinone is obtained by the method of Leuchs, Seeger and Jaegers[1] by oxidation with cold 5 N nitric acid and isolated as its perchlorate. A 0·5% stock solution of the substance is prepared by triturating in an agate mortar 0·5 g. of the solid with the calculated quantity of sodium hydroxide and the solution is made up to 100 ml. This stock solution is found to be stable for a long time but at the end of four weeks it leaves a sediment on the walls of the container. The indicator action of the substance is, however, not affected by this.

The transition interval of the indicator is measured by noting the colour of the indicator in a series of buffer solutions of varying pH values. Such studies have shown that the transition of the indicator takes place over a pH interval of 8·1 to 9·2. Two drops (0·1 ml.) of the 0·5% indicator solution present in 40 ml. of the titrating mixture are found to give a satisfactory colour change in a regular titration and the indicator correction corresponding to this concentration of the indicator is found to be equivalent to 0·05 ml. of 0·1 N sodium hydroxide.

The applicability of the indicator in regular acid-base titrations is studied by carrying out a large number of titrations between (*i*) strong acid and strong base, (*ii*) weak acid and strong base and (*iii*) strong acid and weak base. While the first two gave excellent results (correct to one drop decinormal solution) with sharp end points, the strong acid-weak base titration gave erroneous values. This is understandable as the transition interval of the indicator lies between pH values of 8·1 and 9·2.

As the colours of the indicator on the acid and basic sides have overlapping spectra, we considered it worthwhile to modify the indicator with a blue dye in order to improve the colour change. Copper phthalocyamine tetrasulphonate (potassium salt) formerly employed by Sastry and Pratt[2] is found to be very useful in this regard. A sample of the dye kindly supplied by Messrs. Dupont De Numours and Company is used in our investigations. The