

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

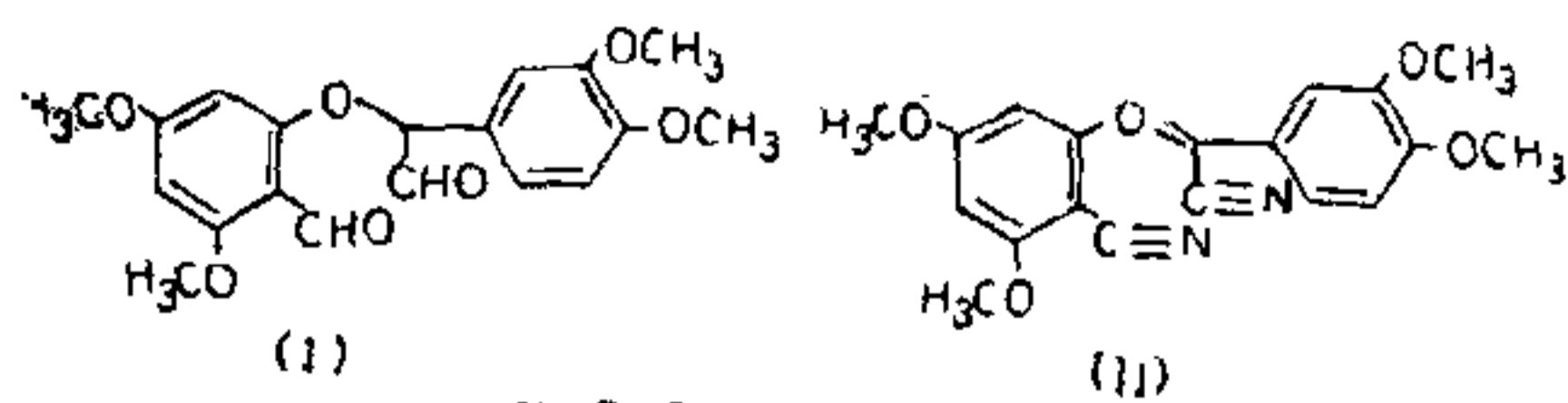


CHART-2

### 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 iodometrically. 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<sub>2</sub>, 8.2%; C<sub>19</sub>H<sub>22</sub>O<sub>7</sub>N<sub>2</sub> requires N<sub>2</sub>, 7.2%).

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Delhi-7, December 9, 1965.

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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<sup>1</sup> by oxidation with cold 5N 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 0.1N 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 phthalocyanine tetrasulphonate (potassium salt) formerly employed by Sastry and Pratt<sup>2</sup> is found to be very useful in this regard. A sample of the dye kindly supplied by Messrs. Dupont De Nemours and Company is used in our investigations. The

dye is stated to be 87.3% pure and we have found that a mixture containing 0.75 ml. of 0.1% dye solution for every 5 ml. of the 0.5% bruciquinone indicator solution gives a sharp colour change from deep pink to green. One drop of this mixture is found to be sufficient for every 40 ml. of the titration mixture in contrast to 2 drops required when bruciquinone alone is employed as indicator.

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Regional Engineering College, P. S. SASTRY.  
P.O. Kazipet, July 27, 1965. M. RAMAIAH.

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### TETRANITROAZOXYBENZENE AND PHOTOINDUCED CONDENSATIONS OF POLYNITROAROMATICS

STENBERG AND HOLTER<sup>1</sup> recently have reported the formation of 3, 5, 3', 5'-tetranitroazoxybenzene (I) by irradiation of 1, 3, 5-trinitrobenzene in ethanol and tetrahydrofuran. They have stated that photo-chemical condensations of polynitroaromatic compounds have not been reported earlier and that (I) was prepared with difficulty by a non-photochemical method.<sup>2</sup>

Photochemical decomposition of polynitroaromatic compounds leading to the formation of azoxy derivatives through intermediate nitroso compounds has already been reported.<sup>3,4</sup> The formation of a dicarboxy derivative of 3, 5, 3', 5'-tetranitroazoxybenzene (II) itself has also been reported by the present authors,<sup>5</sup> by the photochemical condensation of 2, 4, 6-trinitrobenzaldehyde with an intermediate formation of 2, 4-dinitro-6-nitrosobenzoic acid. The identity of 2, 2'-dicarboxy-3, 5, 3', 5'-tetranitroazoxybenzene with the "white compound" formed as a by-product in a continuous TNT manufacture has also been reported. 3, 5, 3', 5'-tetranitroazoxybenzene can be obtained without any difficulty in a good yield by the procedure described below:

10 g. of (II) was refluxed with 100 ml. of pyridine on a sand-bath for 1.5 hours. The black mixture was poured in water and acidified with dil. H<sub>2</sub>SO<sub>4</sub>. The black residue was filtered and washed free of acid. After washing, the residue was dried and extracted with boiling toluene with addition of little animal charcoal. The toluene extract on cooling gave pink-coloured needles of (I). Final crystallisation was from acetic acid.

Yield—5 g., m.p. 190°.

Anal. calcd. for C<sub>12</sub>H<sub>6</sub>N<sub>8</sub>O<sub>9</sub>: Mol. wt., 378, N, 22.22.

Found: Mol. wt., 376, N, 22.26.

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Development Laboratory, S. A. JOSHI.  
Kirkee, Poona-3, July 3, 1965.

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### PROTEOLYTIC ACTIVITY OF SOME PLANT LATEX (Effect of Time Variation)

IN a previous communication<sup>1</sup> we reported the proteolytic activity of fourteen samples of latex collected from different families and species of plants. The pH optima for five of these latices available in appreciable quantities were also determined by employing different buffers at various pH. As a result it was observed that the latices of *Calotropis gigantea* and *Carica papaya* have 6 as their pH optima. In addition, it was found that the latices of *Calotropis procera* and *Cryptostegia grandiflora* exhibited two distinct peaks of activity each at pH 4 & 8 and 5 & 7 respectively. The existence of these two peaks at different pH led us to suggest the presence of two components possessing proteinase activity. The foregoing describes the effect of time variation on the proteolytic activity of five samples tested previously at pH 7.

*Materials.*—Fresh latex was collected from different plants having healthy vigorous growth. Leaves and tender shoots were nipped and the oozing milky sap was allowed to drain in clean dry tubes kept immersed in salt-ice mixture. In cases where yield of latex was scanty, collection was made from more than one plant growing in the neighbourhood and pooled. The best time for collection was found to be early morning before sunrise when the plants were quite turgid and afforded the maximum yield of latex.

*Determination of Proteolytic Activity.*—Proteolytic activity was measured as described by Yamafuji and Yoshihara.<sup>2</sup> The amount of tyrosine released was estimated by the method of Lang and Wegner<sup>3</sup> as described by Turba.<sup>4</sup>

A known volume (0.5 ml.) of latex was diluted to 2 ml. with sodium carbonate (0.2 N)