order rate constants in CAT increased with increasing [substrate] and the second order rate constant calculated as $k_2 = k_1'/[\text{Substrate}]$ gave concordant values establishing a first order dependence to the substrate.

The concentration of NaOH was varied and the rate was found proportional to $[OH^-]^{-1}$. Further, a plot of log k_1' against log $[OH^-]$ gave straight lines with slopes nearly 1. Variations in ionic strength and dielectric constant had negligible effect on the reaction rate. The reactions were carried out at different temperatures (40°–60° C) and energy of activation ($\Delta E^{\neq}$), heat of activation ($\Delta H^{\neq}$) and entropy of activation ($S^{\neq}$) were found to be 11·0, 10·4 and −45; 11·8, 10·8 and −44; and 12·5 Kcal mole^{-1}, 11·4 Kcal mole^{-1} and −42 e.u. for (I), (II) and (III) respectively.

In an aqueous solution, CAT hydrolyses giving several products, *viz.*, *p*-toluenesulphochloramide (CAT'), dichloramine-T, sodium hypochlorite and *p*-toluenesulphonamide. The hydrolytic steps are given in our earlier investigation[7]. In an alkaline media, dichloramine-T does not exist. Out of the remaining three, CAT′ is the only species whose relative concentration decreases with an increase in pH. According to our present investigation therefore CAT′ is the main oxidizing species of CAT.

Following steps are proposed for the oxidation of hydroxybenzoic acids (S) by CAT:

$$CH_3C_6H_4SO_2NNaCl + H_3O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{CAT}}{} \tag{1}$$

$$CH_3C_6H_4SO_2NHCl + NaOH \text{ fast} \underset{\text{CAT}'}{} \tag{2}$$

$$\text{CAT}' + S \xrightarrow{k_2} \text{Intermediate (X)} \ldots \text{slow and r.d.} \tag{3}$$

$$X + \text{CAT}' \xrightarrow{k_3} \text{Products} \ldots\ldots\ldots \text{fast} \tag{4}$$

Applying steady state treatment for CAT′ and X and taking $k_2 \ll k_{-1}$, the rate law derived is:

$$-\frac{d}{dt}[\text{CAT}] = \frac{2k_1k_2\,[\text{CAT}]\,[S]}{k_{-1}\,[OH^-]} \tag{5}$$

This is in agreement with the experimental results.

From Table I the rate follows the order (I) > (II) > (III). This again is in agreement with the values of $\Delta E^{\neq}$. The low rate for the oxidation of (III) as compared to (I) and (II) is undoubtedly due to steric factors involved during intramolecular hydrogen bond formation.

A linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ has been observed[9] and the value of 'β' the isokinetic temperature computed from the slope of the linear plots was found to be 308° K. The value of 'β' calculated by Exner's[10] method was found to be 352° K. Such values have also been obtained for the Pb(IV) acetate oxidation of substituted phenols[11].

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CAROTENOIDS OF *CEPHALANDRA INDICA* (*COCCINIA INDICA*)

It has been reported from this laboratory that lutein is an efficient precursor of dehydroretinol[1–4], which is the predominant form of vitamin A in freshwater fish. It is possible that other carotenoids with a preformed 3,4-dehydro-β-ionone ring or carotenoids which are capable of giving rise, *in vivo*, to carotenoids with at least one 3,4-dehydro-β-ionone ring may also serve as precursors of dehydroretinol in freshwater fish. In search of such carotenoids we were attracted by the colour of ripe fruits of *Cephalandra indica* (local name : Kunduli), which is a popular summer vegetable in Assam. The plant grows widely in Upper Assam region. We, therefore, carried out a quantitative analysis of the carotenoids of the ripe fruits of *Cephalandra indica*.

The sources of chemicals and solvents have been described previously[1–4]. One fresh ripe fruit (10·5 gm) was ground with anhydrous sodium sulphate in a glass mortar and the dry red powder was extracted

with small portions of peroxide free diethyl ether. The extraction was repeated until the extracts were colourless. The pooled extract was concentrated by distillation under reduced pressure. The red residue was dissolved in a minimum volume of light petroleum containing a few drops of diethyl ether. The extract was subjected to t.l.c. as follows : the solution was applied as strips to six silica gel G plates (0·25 mm thickness, 20 × 20 cm). Light petroleum (b.p. 60–80° C) and acetone (19 : 1 vol/vol) mixture was used as the solvent system. The carotenoids separated into six bands. The bands were then quickly transferred by scrapping into six 50 ml conical flasks each containing about 20 ml of peroxide free diethyl ether. The extracts were filtered and evaporated to dryness *in vacuo*. The residues were dissolved in light petroleum. The spectroscopic and chromatographic properties of the different carotenoids are shown in Table I.

sample of lycopene isolated from tomato[6]. Small amounts were isolated of a compound with an absorption spectrum (λ_{max} in light petroleum at 420, 450, 476 nm) and chromatographic behaviour typical of cryptoxanthin. For further characterisation this was co-chromatographed with cryptoxanthin isolated from papaya[7] on silica gel G plates.

The carotenoid in fraction 5 was characterised as apo-6′-lycopenal from its visible absorption spectrum (λ_{max}. 468 nm in light petroleum and 475 in ethanol), i.r. spectrum ($\nu_{max}^{n\text{-}hol}$ 1680 cm^{-1}) and by co-chromatography with a sample of apo-6′-lycopenal isolated from tomato[8]. The identity was further confirmed by reducing it with $NaBH_4$ when apo-6′-lycopenol, λ_{max} 420, 446, 470 nm in light petroleum was obtained[8].

The carotenoid in fraction 4 could not be characterised with certainty, but resembled apo-6′-lycopenal in its visible spectrum. It formed a distinct band from apo-6′-lycopenal during t.l.c. on silica gel G. That it was an aldehyde was confirmed from its i.r. spectrum and by reducing it with $NaBH_4$ when a carotenoid with λ_{max}. 420, 446, 470 nm in light petroleum was obtained.

TABLE I

Spectroscopic and chromatographic properties of the carotenoids of Cephalandra indica

Fraction No.	R_f in light petroleum (60–80° C) and acetone (19 : 1 vol/vol)	λ_{max} in light petroleum (60–80° C) (nm)	Co-chromatography with	Identification	Amount** mg/100 g (fresh)
1	0·78	420, (450), 476	Synthetic -βcarotene	β-carotene	2·24
2	0·72	444, (470), 500	Lycopene from tomato	Lycopene	5·68
3	0·52	420, (450), 476	Cryptoxanthin from papaya	Cryptoxanthin	0·46
4	0·178	468	..	..	1·68
5	0·176	468	apo-6′-lycopenal from tomato	apo-6′-lycopenal	1·67
6	0·0	Diffused	..	..	..

* λ_{max} value in brackets indicates maximum absorption.

** Calculated on the basis of $E_{1\,m}^{1\%}$ value of 2592 at 450 nm for β-carotene, 3450 at 470 nm for lycopene, 2460 at 450 nm for cryptoxanthin and 2450 at maximum absorption for the fourth and fifth fractions.

The carotenoids were characterised by comparing the physical properties from the table for the identification of the carotenoid pigments[5]. Fraction 1 was characterised as β-carotene by study of its spectroscopic properties and co-chromatography with a synthetic sample of β-carotene. Fraction 2, which constituted the major pigment of the fruit, was characterised as lycopene. The absorption maxima in different solvents agreed well with those reported for lycopene and the spectroscopic properties of this fraction were found to be identical with those of a

It can be seen from Table I that the fully ripe *Cephalandra indica* fruit is very rich in lycopene (5·68 mg/100 g of fresh fruit) and in this respect it can be very well compared with tomato, which is regarded as the richest source of lycopene.

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MOLECULAR POLARIZABILITIES OF SOME HALOGENOANILINES AND N,N-DIMETHYLANILINES

RECENTLY Lippincott and Stutman[1] have proposed the use of a semi-empirical δ-function model for the calculation of molecular polarizabilities. The δ-function model has been applied by several workers[2–8] for different systems. The molecular polarizability can also be obtained from the experimentally obtained molar refraction of the system by the Lorentz–Lorenz equation In this note, we have calculated the polarizabilities of some halogenoanilines and N,N-dimethylanilines with a view to testing the applicability of the δ-function model and compare the results with those obtained from the measured molar refractions[9].

The mean molecular polarizability is given by the expression

$$\alpha_M = \tfrac{1}{3}\left[\Sigma a_{\parallel p} + \Sigma a_{\parallel n} + \Sigma 2a_{\perp}\right] \qquad (1)$$

where $\Sigma a_{\parallel p}$ and $\Sigma a_{\parallel n}$ are the contributions from bond region electrons and non-bond region electrons respectively to the bond parallel polarizability and $\Sigma 2a_{\perp}$ is the sum of the bond perpendicular contribution.

The bond region electron contribution to parallel polarizability after introducing the polarity correction is calculated using linear combination of atomic δ-function wavefunction[1] and is given by

$$a_{\parallel p} = \frac{4nA_{12}}{a_0}\left[\frac{R^2}{4} + \frac{1}{2C_{R12}^2}\right] \times \exp\left[-\tfrac{1}{4}(X_1 - X_2)^2\right] \qquad (2)$$

where $A_{12} = (A_1A_2)^{1/2}$, A being the δ-function strength determined from reduced electronegativity of the atom, a_0 is the radius of the first Bohr orbit and n is the bond order. R is the internuclear distance at equilibrium configuration and

$$C_{R12} = (n_1n_2N_1N_2)^{1/4}\ (A_1A_2)^{1/2}$$

where n_i $(i = 1, 2)$ is the principal quantum number of the valence shell and N_i is twice the column number in the periodic table. X_1 and X_2 are the electronegativities of the atoms 1 and 2 respectively on the Pauling scale.

The non-bond region electron contribution is takeu from Linnett[10] as

$$\Sigma a_{\parallel n} = \Sigma f_i a_i \qquad (3)$$

where f_i is the fraction of valence electrons in the ith atom not involved in bonding and a_i is the atomic polarizability of the atom.

The perpendicular component as given by Lippincott and Stutman[1] is

$$\Sigma 2a_{\perp} = n_{df}\frac{\Sigma x_j^2 a_j}{\Sigma x_j^2} \qquad (4)$$

where $n_{df} = (3N\text{–}2nb)$ is called the residual atomic polarizability degrees of freedom.

For the calculation of molecular polarizabilities of halogenoanilines and N,N-dimethylanilines the equations (1)–(4) have been employed. The atomic polarizabilities and δ-function strengths are taken from Ref. 1 and the structural data from Refs. 11 and 12. The electronegativity values are taken from Durrant and Durrant[13]. The calculated A values and C_{R12} values for various bonds are given in Table I. The n_{df} values for anilines and N,N-dimethylanilines are taken as 20 and 26 respectively.

TABLE I

Delta function strengths A's (in 10^8 cm^{-1}) and C_R's (in 10^8 cm^{-1}) of bonds

	Bond						
	C–C	C–H	C–N	C–F	C–Cl	C–Br	C–I
A	1·5989	1·7384	1·6737	1·7940	1·5086	1·3831	1·3285
C_{R12}	3·3958	4·1346	7·0790	8·2536	7·6805	7·5670	7·6852