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CONTENTS

A FEW ASPECTS OF MAGNETIC STUDY OF CHEMICAL COMPOUNDS

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The study of the magnetic properties of chemical compounds began with Faraday more than a century ago. The theoretical explanations have been formulated one after another by Langevin, Curie, Weiss, Stoner and VanVleck But the applications of the results to structural chemistry started in 1920 when Lewis first formulated a relationship between atomic magnetic moment and chemical valence. This led to further applications of the results to various aspects of molecular structure. It is the intention of the author to trace the development of one method towards the study of certain aspects of molecular structure.

General Experimental methods

Any substance placed in a magnetic field develops an induced moment and if the field is uniform the specimen will experience an orientation effect due to the anisotropic nature of the body. The magnetic moment so acquired will be proportional to the volume susceptibility of the substance. On the other hand if the field is non-uniform, the specimen will experience a displacement force which may be expressed as

$$f = \mathrm{K\,V\,H}\,\frac{d\,\mathrm{H}}{d\,\mathrm{S}}$$

It is this property of the substances in a non-uniform field and this fundamental equation for the force experienced form the basis for the measurement of susceptibility of different substances by different methods. Three general methods are most commonly employed with progressive modifications to aim at greater accuracy and reliability. They are (1) Quincke's method for liquids, (2) Guoy method suitable mostly for liquids and solids in certain states and (3) Curie torsion method which is suitable for liquids and solids particularly when available in small quantities.

A very useful preliminary study for applying the magnetic methods to molecular structure of chemical compounds is the study of ions. The general method adopted for the evaluation of ionic susceptibilities is based on the

principle that the molar susceptibility of a truly ionic compound is the sum of the susceptibilities of the constituents.

$$\chi_M = \chi_{cation} + \chi_{anion}$$

Different authors employed different methods for the evaluation of ionic susceptibilities both theoretically and experimentally. The values given by different workers differed, and in some cases by such large amounts that these methods require a critical analysis.

The first method is by the use of Halogen acid measurements. Hydrogen ion H^+ has no orbital electrons and hence in its free state it should have zero magnetic susceptibility. On this basis Reicheneder [1] assumed hydrogen ions to behave as free particles in aqueous solutions of halogen acids. Hence he attributed the entire susceptibility of the halogen acids in aqueous solution to the halogen ion F^-, Cl^-, Br^- etc. Thus by studying the halogen acids in aq. solutions the values for the halogen ions have been evaluated.

TABLE-I

Ion.	Molar sus. Halogen acids.			χ Ion. Mean.
	Reicheneder[1]	Kido[2]	Farquharson[3]	
Chloride	21·9	21·9	23·0	22·3
Bromide	32·5	34·6	31·4	32·8
Iodide	50·2	53·5	49·3	49·9

In 1930 Weiss [4] pointed out that the hydrogen ion H^+ in solution should have a strong polarising effect on the solvent molecules due to the intense electric fields surrounding this ion and hence changing their magnetic susceptibilty Using the data of Fajans and Joos [5] for the amount by which the presence of small cations changes the refractivity of pure water Weiss has calculated the corresponding changes in diamagnetic susceptibility (Table II).

1. Reicheneder, Ann, Physik, **3**, 58 (1929).
2. K. Kido, Sci. Rep. Tohoku Univ., P. 149, (1932).
3. J. Farquharson, Phil. Mag., 283 (1931)
4. P. Weiss, J. Phys., **1**, 185 (1930) ; Compt rend. **190**, 95 (1930).
5. K. Fajans and G. Joos, Z. Physik, **23**, 1, (1924).

TABLE — II

Change of Molar susceptibility of water due to presence of dissolved cations (Paramagnetic effect).

H^+	1·1	Mg^{++}	3·2
Li^+	0·9	Ca^{++}	1·1
Na^+	0·5	Sr^{++}	0·9
K^+	0·0	Ba^{++}	0·0

The data in Table II show an effective paramagnetism for all small cations when present in a solvent like water. Thus the halogen ion susceptibilities as deduced from the measurements of halogen acids will all be greater than if the H^+ ion were assumed devoid of magnetic effect.

Thus Weiss calculated the value for the chloride ion from acid value allowing for H^+ contribution and using this as the starting point for alkali ions from the experimental values of different authors for the alkali halides. These values are shown in Table III.

TABLE — III

	χ ion.		Li + standard.	
Ion.	Weiss Pascal	Weiss Hocart	Brindley[6] & Hoare.	Kido.
Fluoride	—	—	9·4	12·2
Chloride	23·1	23·1	24·2	22·1
Bromide	34·7	33·9	34·5	34·7
Iodide	49·8	49·5	50·6	53·2
Li^+	—	—	0·7	—
Na^+	7·6	8·2	6·1	7·6
K^+	16·0	16·5	14·7	13·6
Rb^+	24·3	—	22·0	27·2
CS^+	41·0	—	35·1	41·0

6. G. W. Brindley and F. F. Hoare ; Proc. Roy. Soc ; A. 152, 342 (1935)

On the theoretical side it was Langevin[7] who first deduced the classical formula for the diamagnetic susceptibility of spherically symmetrically atom.

$$\chi_M = -\frac{e^2}{6mc^2} \Sigma \bar{r}^2$$

where $\bar{r}^2$ is the time average of r^2, r being the distance of the electron from the nucleus the summation extending over all circum nuclear electrons. With the introduction of Quantum mechanics various methods of calculating $\Sigma \bar{r}^2$ have been suggested. Pauling[8] was the first to suggest an extensive computation. Hartree[9] and Stoner[10] dealt with this problem from the point of view of the distribution of electron density in a spherically symmetrical atom or ion. A great impetus to the study was given by Slater[11] who gave rules for the calculation of $\bar{r}^2$ for each electron. Brindley[12] calculated using Slater's method the susceptibilities of a large number of ions. But these theoretically calculated values were numerically greater than the experimental values. Angus[13] modified Slater's method by treating separately the S and P electrons having the same principal Quantum number. For many ions better values were obtained with this modification.

Joos considered that the contribution to the total susceptibility of anion and cation in ions of inert gas configurations (i. e.)

Na F
K Cl
Rb Br
CS I

} are inversely as the square of the nuclear charge.

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7. Langevin, Ann. Chim. Phys., 4, 678 (1905).
8. Pauling, Proc, Roy. Soc., **114A**, 181 (1927)
9. D. R. Hartree, Proc. Cam. Phil. Soc., **24**, 89 and 111 (1928)
10. E. C. Stoner, Proc. Leeds. Phil. Soc., **1**, 484 (1929)
11. J. C. Slater, Phy. Rev., **36**, 57 (1930)
12. G. W. Brindley, Phil. Mag., **11**, 786 (1931).
13. W. R. Angus, Z. Physik., **82**, 759 (1933) ; Proc. Roy. Soc., **136A**, 569 (1932)

Brindley[14] improved upon this and showed that it is more accurate to express the ratio as

$$\frac{1}{(Z-S)^2} : \frac{1}{(Z^1-S^1)^2}$$

where Z and Z^1 are the nuclear charges and S and S^1 are Slater's screening constants in the calculation of atomic susceptibilities. The values for the salts and for the ions calculated on this basis is given in Table IV.

TABLE — IV

Salt with inert gas configuration.	Expt. value by Brindley.	Susceptibility Ionic Cation	Anion.
Na F	15·9	5·4	10·5
K Cl	38·8	15·0	23·9
Rb Br	56·4	22·2	34·3
CS I	85·7	34·6	51·1

A comparison of the values in Tables III and IV shows fairly large differences for certain ions.

Hoare and Brindley[6] later proposed a slightly different set of standard ionic values based on the assumption that in the case of the lightest ion of the alkali series, Lithium, the experimental susceptibility might be taken as the same as the theoretical value calculated by Slater's method. Since the theoretical value for this ion is small ($\chi M = -0 \cdot 72 \times 10^{-6}$) any small divergence between the theoretical and experimental values will not appreciably influence the values for the other ions derived from this starting point. This method is open to objection that the choice of Li as standard is not an ideal one since for very light ions it has been shown that the theoretical susceptibilities are considerably low. The theoretical and experimental values approach each other for ions having

14. G. W. Brindley, Phil. Mag., **11**, 786 (1931).

atomic number greater than **14**. But the only consolation with Li^+ being used as standard is that its value itself is very low and even if there is a discrepancy it should necessarily be very low. Values obtained on this basis are given in column 4 table III.

Kido [2] has suggested another approach to the problem. From a large number of measurements of the Molar susceptibilities of polar salts he has plotted curves in which salts in the same group of the periodic table with a common anion are compared. When the molar susceptibility is plotted against the number of electrons in the cation for series with the same anion Kido finds that a series of straight lines result. In this way the alkali halides give a set of parallel st. lines. By extrapolation to the value effective atomic number 0, he deduced the value for the anion assuming that the susceptibility of the hydrogen ion is zero (i. e.) the extrapolated value is corresponding to the acid $H^+ \bar{A}$ and taking H^+ as zero gives the anion value required.

This method is open to two objections. First the effective paramagnetism of the hydrogen ion should be taken into account. Secondly the experimental susceptibilities as well as theoretical values are not linear with the number of cations or anions. The only redeeming feature in Kido's results is that for the alkali halides the divergence from linearity is not large. But when we pass on to salts containing complex ions this method breaks down.

A comparison of the results of these various methods show a remarkable agreement in the case of chloride, bromide and iodide ions. For fluoride the values are very limited and the agreement is not so good. A mean of these values is given below for these ions and these could be taken as standard values for the determination of the ionic susceptibilities for other ions.

TABLE — V

Fl^-	$9{\cdot}1 \pm 1{\cdot}8$	mean of 3 values.
Cl^-	$23{\cdot}4 \pm 1{\cdot}3$	,, 7 ,,
Br^-	$34{\cdot}6 \pm 1{\cdot}6$	,, 7 ,,
I^-	$50{\cdot}6 \pm 1{\cdot}6$	,, 6 ,,

The values of the alkali ions are also a little restricted and the agreement is not as good as for halide ions. The mean values for these ions are

TABLE — VI

Na^+	7·0 ± 1·7	mean of 5 values
K^+	15·1 ± 1·4	,, 5 ,,
Rb^+	22·8 ± 1·5	,, 3 ,,
CS^+	37·8 ± 3·3	,, 4 ,,

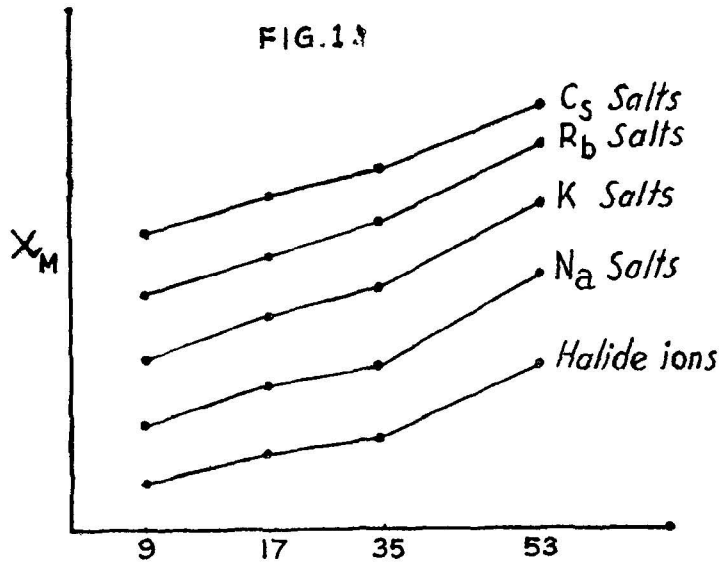
V. C. G. Trew[15] made use of all the available values for the alkalihalides and the summarised values of the halide ions to evaluate the values for the alkali ions by a graphical method. The values of the sodium salts are plotted against the number of electrons in the anions. Similar graphs are drawn for K, Rb and CS halides. These graphs are not linear but they are nearly parallel over the corresponding section on passing from one halide value to the next. This graphical representation serves as a check on the accuracy of the experimental figures as well as a means of smoothing out any individual deviations for a given compound. In the same graph below the graphs for the halide salts values of the halide ions are similarly plotted.* The susceptibility for the various alkali ions are given by the average distance between the graphs for the corresponding parallel sections.

Thus a new standard of Alkali ion values are obtained.

TABLE — VII

Na^+	=	6·8
K^+	=	14·9
Rb^+	=	22·5
CS^+	=	35·0

FIG. 1



15. V. C. G. Trew., Trans. Faraday. Sec., **37**, 482 (1941).

As far as Li^+ value is concerned, it is small and is difficult to estimate it correctly by these methods. Hence it is taken as ·7 assuming an agreement between theoretical and experimental values.

These ionic values can be used as standard values to obtain ionic susceptibility values for other ions [16] provided that polar salts are used and the susceptibility is assumed additive. Thus the values for the univalent nitrate, sulphate, carbonate ions have been evaluated.

So far the influence of the deforming power of ions on each other when they combine to form compounds has not been taken into account in the estimation of ionic susceptibilities. *Flordal and Frivold* [17] showed that large changes of susceptibilities took place when some alkaline earth halides were dissolved in water. Hocart [18] obtained a 2% increase of susceptibility on dissolving calcium chloride in water. The influence of deforming power of ions on magnetic susceptibilities has been considered at length by Varadachari [19] and Subramaniam [20]. Fajans [21] *has shown that the deforming power of the cation is large when its size is small and charge great. Ions possessing inert gas configurations produce less deformation than those which do not possess such closed configurations. Anions on the other hand suffer much deformation when both their charge and size are large.* These conclusions were shown to be applicable in the case of some metallic halides by Subramaniam [20]. It is hence clear that in the estimation of the susceptibilities of free ions, a careful investigation of ionic deformation and the consequent departure from the law of additivity must be made in every case. That this is necessary is shown by the fact that Subramaniam [20] obtained as much as 22% increase in susceptibility on dissolving *cadmium iodide* and 11% increase on dissolving *zinc iodide* in water.

Hence one method of studying ionic deformations is to determine the susceptibilities of salts in the solid state and in the state of solution. Any change in the susceptibility may be attributed to the release of ionic deformation. Besides there is the effect of hydration of ions in solution. The ions may attach themselves to solvent molecules bringing about new constraints. But careful

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16. V, C. G. Trew, Trans. Faraday, Soc., **37**, 476 (1941).
17. M. Flordal and O. E. Frivold, Ann. Physik, **23**, 425 (1935),
18. Hocart, Compt. Rond., **188**, 1151 (1929).
19. P. S. Varadachari, Proc, Indian, Acad. Sci., **2A** 16 (1935)
20. K. Subramaniam, Ibid **4A**, 404 (1936)
21. K. Fajans, Radio element and Isotopes, p. 74 (1931).

investigations of Hocart, Flordal and Frivold and Subramanian indicate that such interaction in the solution does not cause a great change in the susceptibility.

The problem becomes more complicated when we proceed to determine the ionic susceptibilities of complex radicals. In salts formed by the combination of a simple ion with a complex radical, we have to consider not merely the electronic interactions within the radical but also the constraints that may be formed or released due to the presence of the simple ion. Therefore when such *salts are dissolved in water, the changes observed would depend on the nature of the dissociation, the formation of polymers and the release of deformation of the electronic system within the molecule.* Rao and Sriraman[22] have studied several salts containing a few complex acid radicals both in the solid and solution states and found appreciable deviations from addivity law when the salts go into solution.

TABLE — VIII

Substance.	χ M Solid State.	χ M Dissolved State.
HIO_3 Iodic acid	46·9	41·3
$LiIO_3$ Lithium iodate	48·4	41·8
KIO_3 Potassium iodate	59·6	56·0
$NaNO_2$ Sodium Nitrate	14·5	17·6
KNO_2 Potassium Nitrate	23·3	27·0
$NaNO_3$ Sodium Nitrate	25·0	26·4
Na_2SeO_3 Sodium Selenite	51·8	59·6

22. Rao and R. Sriraman, Phil, Mag., **24**, 1025 (1937).

Mata Prasad[23] and his coworkers have by a graphical method found the susceptibilities of some metallic ions and a large number of organic acid radicals and concluded that the ionic value for a given radical depended upon the particular group of metals with which it is in combination. Their results show that the susceptibility values for the anions deduced from the salts of Mg, Zn, and cadmium are distinctly different from those deduced from the salts of calcium strontium and barium. This means that the susceptibility of the anion is constant only for cations of a particular subgroup in the periodic table. They also pointed out that the susceptibility of a cation is not a constant quantity but is different in combination with different organic anions. These differences are quite large in some cases and small in others.

TABLE — IX

	Anion.	Graphical. χ Anion		χ Anion
		Li, K, Na.	Ca, - Sr, - Ba.	Additive.
1.	Formate	20·50	15·00	17·30[22]
2.	Acetate	34·00	25·00	29·80[22]
3.	Oxalate	34·40	34·00	33·86[25]
4.	Succinate	58·80	36·00	55·67[24]
5.	Salicylate	81·00	74·50	74·62[24]
6.	Malonate	45·00	53·00	..
7.	Stearate	206·00	212·00	..

23. Mata Prasad et. al.,
    (*a*) Proc. Ind. Acad. Sci., 16A, 307, (1942).
    (*b*) *ibid.*, 20A, 224, (1944).
    (*c*) J. Chem. Phys., 17, 819 (1949).
    (*d*) *ibid.*, 18, 936, (1950).
    (*e*) *ibid.*, 18, 94, (1950).
    (*f*) *ibid.*, 20, 129 (1952).
24. S. Sriraman & S. R. Thiruvengadathan, Bull. Chem. Soc., Japan, 34, 1560 (1961).
25. Venkateswarlu and Sriraman, Trans. Faraday Soc., 53, 438 (1957).

When two ions combine there is every likelihood of a deformation taking place in both the ions. It is quite possible that the degree of deformations in ions may be different for the different groups of cations. To what extent this will affect the susceptibility of the anions is a question which is worth considering. Sriraman and Thiruvengadathan [24] studied a few complex ions and calculated the anion values on the basis of Pascal's additive law.

TABLE-X

Ion.	Mean value from Salts.	χion from acids.	Mean
Benzoate $C_7H_5O_2$	69.11	71.27	70.19
Salicylate $C_7H_5O_3$	75.17	73.59	74.38
Propionate $C_3H_5O_2$	44.39	43.67	44.03
Butyrate $C_4H_7O_2$	49.74	54.15	51.95
Succinate $C_4H_4O_4$	53.68	56.73	56.21

It is interesting to compare these values with the values (Table IX) obtained by Prasad and Co-workers by graphical method on the basis of linearity. For four ions the values from alkali salts are larger than from alkaline earth salts, for the last two ions, the change is the other way about and for the oxalate ion no change is observed. If the values of the various ions are calculated on the basis of additivity such marked variations are not found. Trew [16] has pointed out that the graphs drawn by Mata Prasad and co-workers do not show linearity and the points do not lie on a single straight line. The investigation carried out by Sriraman and Thiruvengadathan also confirm this point. So, in general it can be calculated, from the literature available on the subject, that the additivity method of evaluating the ionic value is more reliable subject to the accuracy of measurement and the small error involved in the assumption of cation values.

ON THE EARLY EXHIBITION OF HETEROSIS IN TWO BRINJAL HYBRIDS *

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In certain crosses, heterosis may be exhibited quite early. Kakizaki (2) recorded that hybrid seeds of brinjal (*Solanum melongena* L.) were heavier than those of the parent lines. Pal and Singh (4) as well as Capinpin and Alviar (1) found that hybrid brinjal seeds had a higher germination percentage. The present study was taken up primarily to find whether the hybrid brinjal seedlings emerged earlier, since there appeared to be no previous report on the subject. Heterosis affecting seed weight, germination percentage and seedling height were also recorded.

MATERIALS AND METHODS

The hybrids studied were two reciprocal crosses, namely (i) Black Beauty x New Hampshire (ii) New Hampshire x Black Beauty. The parent lines were studied for comparison with hybrids.

Earliness of Emergence: Kotowski's (3) method of coefficient of velocity of germination was used for this study. Steam sterilized coarse sand was placed in a green house flat to a depth of 5 cm. Furrows were formed in the sand 5 cm apart and 2 cm deep. Random samples of one hundred seeds each, from the hybrid seed lots and parent lines were sown in separate furrows. The seeds were covered with sterilized sand so that they were at a uniform depth of 2 cm. The flat was kept on a green house bench, maintained at 65°F, and watered as needed to keep the optimum moisture level. The flat was examined at 24 hour intervals and the day of first emergence of seedling was recorded.

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* These studies were conducted by the author at the University of Tennessee, Knoxville, Tenn., U. S. A. during 1960.

Each day the seedlings were picked away as they emerged from soil and the number recorded. The observations were made for fifteen days. The coefficient of velocity of germination was calculated according to the formula

$$C.V. = \frac{100 \times A_1 + A_2 \ldots\ldots Ax}{A_1 T_1 + A_2 T_2 \ldots\ldots Ax\ Tx}$$

A = the number of seedlings picked out.

T = the number of days after sowing corresponding to A.

The coefficients of the hybrids were compared with those of the parent lines. The germination percentages were also compared. The day of maximum emergence was recorded.

Seed weight: Three random samples of one hundred seeds each were taken from the seedlots of the hybrids and parent lines. Their weights were recorded in mg. The average of each hybrid was compared with the averages of the parent lines for indication of heterosis affecting seed weight.

Seedling Height: In another green house flat, seeds were sown and germinated as per the procedure described above. Then the seedlings were thinned out so that they were spaced half inch within the row. 45 days after sowing, twentyfive seedlings, selected at random from each of the lots, were measured and the heights recorded in inches. The averages were calculated. Since the growth was on sterile sand, any superior growth found in the hybrids could be solely attributed to heterosis.

RESULTS AND DISCUSSION

Velocity of Germination and Germination percentage: The results of the germination study are presented in Table I.

TABLE — I

Seed Germination of Black Beauty, New Hampshire and their reciprocal crosses:

	Parent lines		Hybrids	
	Black Beauty	New Hampshire	B. Beauty X N. Hampshire	N. Hampshire X B. Beauty
No. of day for first seedling emergence	6	6	6	6
No. of day on which maximum emergence occured with percentage of emergence	10 (42%)	10 (63%)	6 (39%)	6 (35%)
No. of day on which last seedling emerged	14	13	11	10
Percentage germination	83	94	95	96
Coefficient of Velocity of germination	10·1	9·7	14·0	14·5

All counts of days are from sowing date.

Number of seeds sown in each was 100.

It is seen from the table that both the crosses had a higher coefficient of velocity of germination than the parent lines. They also germinated earlier because the maximum number of seedlings emerged on the very first day of emergence, *viz*,, the sixth day after sowing. But in the case of both the parent lines the maximum emergence was on the 10th day. The germination

percentages of the crosses is not much different from that of New Hampshire, but decidedly greater than that of Black Beauty. The data clearly indicate heterosis in the velocity of emergence.

Seed Weight : The data on the seed weights are presented in Table II.

TABLE — II

Seed weights of Black Beauty, New Hampshire and their reciprocal crosses:

	Weight of 100 seeds in mg.			
	Replications			Mean
	I	II	III	
Black Beauty	462.2	418.4	448.6	443.1
New Hampshire	525.6	531.3	477.2	511.4
B. Beauty x N. Hampshire	584.2	584.4	587.8	585.5
N. Hampshire x B. Beauty	496.3	490.4	502.2	496.5

Based on the means in Table II, the seed weights of the hybrids are compared against the parent line in Table III.

TABLE-III

Comparison of seed weights of two brinjal varieties and their reciprocal crosses

	Mean wt. of 100 seeds in mg				% difference in wt. compared with		
	Of the cross	Of the female parent	Of the male parent	Mean of the parents – mg	Female parent	Male parent	Mean of parents
B. Beauty x N. Hampshire	585.5	443.1	511.4	477.3	+32.14	+16.72	+22.67
N. Hampshire x B. Beauty	496.5	511.4	443.1	477.3	— 2.91	+12.05	+ 4.02

It is seen from the Tables II and III that between the parent lines, New Hampshire had heavier seeds than Black Beauty. The cross involving Black Beauty as the pistillate parent produced heavier seeds than the reciprocal. Between the two crosses, heterosis was more evident in Black Beauty x New Hampshire than in the reciprocal, since the seed weight exceeded not only the parental mean, but also that of the heavier parent.

Seedling Height: The average height of the seedlings, measured 45 days after sowing, are compared in Table IV.

TABLE-IV

Comparison of seedling heights of two brinjal varieties and their reciprocal crosses

	Average height in inches	% difference of the crosses over the mean of parent lines
Black Beauty	1.1	
New Hampshire	0.7	
Mean	0.9	
B. Beauty x N. Hampshire	1.3	44.4
N. Hampshire x B. Beauty	1.4	55.5

25 seedlings were measured in each case.

The data in Table IV indicate that the hybrid seedlings were taller than the tall parent *viz.* Black Beauty, thereby giving clear evidence of heterosis.

SUMMARY

A comparative study of two brinjal varieties, Black Beauty and New Hampshire and the two reciprocal crosses was made to examine the velocity of germination, germination capacity and seedling height. The study indicated the existence of considerable hybrid vigour in both the crosses. The hybrids were superior to the parent lines with regard to all the characters in question. There was no great difference between the two crosses except in seed weight in which case Black Beauty x New Hampshire was superior to its reciprocal cross.

ACKNOWLEDGMENTS

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STUDIES ON THE PROPERTIES OF *XANTHOMONAS CITRI* AND *X. MALVACEARUM* ISOLATES RESISTANT TO STREPTOMYCIN

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One of the limitations in the use of new drugs and antibiotics for plant disease control is development of resistance to the chemicals in the plant pathogenic organisms. Rangaswami (1957) has reported on the development of resistance to streptomycin in *Xanthomonas citri* (Hasse) Dowson and *X. malvacearum* (E. F. Smith) Dowson, the former causing canker disease of citrus and the latter the blackarm disease of cotton. In the present report further studies on the development of resistance to streptomycin in the two plant pathogenic bacteria are detailed.

MATERIALS AND METHODS

The organisms *X. citri* and X. *malvacearum*, were isolated by the tissue culture method from freshly collected diseased leaves of the respective hosts. The isolates were purified either by the single colony method or by the streak dilution method. Pure cultures of the bacteria were maintained on yeast extract glucose agar and used throughout these studies.

Isolation of mutants of X. citri and X. malvacearum: Streptomycin sulphate (Glaxo Laboratories with 745 I U/mg activity) were used for obtaining the mutants in all these studies. Fresh isolates of *X. citri* and *X. malvacearum* were grown in media containing increasing concentrations of streptomycin by means of successive transfers, *viz.*, 25, 50, 100, 250, 500, 800, 1000, 1500, 2000, 2500, 3000 and 4000 mμ/ ml. In the media with lower concentrations of the antibiotic fairly good growth was obtained within 2 or 3 days of inoculation, but with the increase in streptomycin concentration in the medium the growth was slow and so the transfers were made after an interval of 10 days. Resistant bacterial cells of *X. citri* and *X. malvacearum* were obtained from the medium containing 2500, 3000 and 4000 mμ/ml. of streptomycin were isolated and sub-cultured on yeast extract glucose agar. They were numbered and studied for their morphological, biochemical and pathogenic properties as compared to those of the parent isolates.

Inoculation studies: In order to test the pathogenicity and virulence of the bacterial isolates wound inoculations were made with 48 hr. cultures of the test bacterium; wounding was done using finely ground and sterilized carborendum powder. The place of inoculation was later covered with a bit of sterile cotton-wool. On inoculation the plants were incubated in humid chambers and periodical observations were made. Wherever there were positive infections, the pathogen was reisolated from a place away from the point of inoculation and the reisolate was compared and verified with the original isolate.

The bacterial isolates were studied for their morphological, cultural and biochemical properties following the procedures described by Dowson (1949).

EXPERIMENTAL RESULTS

Comparative Study of Morphological and Biochemical Properties of the Isolates of *X. Citri.*

Morphological Characters: The mutant isolates (Xc_1, Xc_2, Xc_3) as well as the parent isolate (Xc) are motile rods with rounded ends and with single polar flagellum. They occur singly or in short chains and shape varies from a short ellipsoidal form to typical rod. Significant variations in the cell size of the isolates Xc 1, Xc 2 and Xc 3 were observed, sometimes their length being two to three times more than that of the parent cells. All the four isolates are Gram negative in reaction and capsulated. Slight changes were noted in the pigmentation; the pigments produced by the isolates Xc 1, Xc 2 and Xc 3 were comparatively paler yellow than the parent culture.

Biochemical Properties: The results obtained in the comparative studies of the biochemical properties of the four isolates of *X. citri* are presented in Table 1.

The results on the production of ammonia, indole and H_2S were almost alike in the case of resistant isolates as well as the parent one, except that the amount of production varied slightly. There were no differences in the lipolytic activity. Significant differences were, however, observed in the methyl red and V, P. tests. The Xc parent isolate was positive to M. R. test while the Xcl gave negative reaction. In the V. P. test the parent and *X*CI isolates gave positive results, while Xc2 and Xc3 isolates were negative in reaction. In their capacity to reduce litmus milk the four isolates were almost similar but the quantities of acid produced in the medium varied with the isolates. The isolates

differed much in their capacity to reduce the nitrate. The parent isolate was incapable of reducing nitrate to nitrite whereas the nitrate was reduced by the Xc1 isolate, while the isolates Xc2 and Xc3 reduced the nitrate only partially.

Utilization of various carbon sources: The results obtained on the comparative studies on the utilization of various carbon sources by the bacterial isolate are presented in Table 2.

Of the ten carbon sources tried Xc1, Xc2 and Xc3 were found to utilize only glucose, xylose and maltose. Xc1 was found to grow comparatively faster in mannitol, xylose, rhamnose and in lactose, while Xc2 grew faster only in rhamnose and Xc3 grew faster in all the carbon sources tested except in sorbitol, mannitol, rhamnose and lactose. Regarding production of acid and gas in the media, all the three resistant isolates were almost identical.

Utilization of various nitrogen sources: The results obtained on the studies on utilization of various nitrogen sources by the four isolates are presented in Table 3.

Though the parent isolate was found to utilize all the nitrogen sources tested except leucine, the rate of growth was not appreciable. Xc1 was found to be a fast grower in media with leucine, tryptophane, histidine, arginine, ammonium sulphate and potassium nitrate, but comparatively slowly in glumatic acid. Xc2 was a fast grower in tryptophane, histidine, arginine, sodium nitrite and potassium nitrate but grew only moderately in all the other sources except the leucine where the growth was very poor. Xc3 was a fast grower in tryptophane, histidine and arginine and a moderate grower in leucine, glutamic acid, creatinum, sodium nitrite and potassium nitrate.

Comparison of the virulence: Actively growing bacterial isolates, Xc1, Xc2 and Xc3 were inoculated on the healthy tender leaves of one month old citrus seedlings, according to the procedure mentioned under Methods and Materials. Periodical observations were made on the number of leaves infected. The results are presented in Table 4.

The results indicate that all the three isolates are pathogenic on the citrus leaves and that no significant variation in their virulence as compared to the parent isolate was noticed. Wherever positive infections were obtained the bacteria were reisolated, compared with those of the respective original isolates and were found to be identical.

Comparative Study of Morphological and Biochemical Properties of the Isolates of *X malvacearum*

Morphological characters: The parent (Xm) and the mutant (Xml, Xm2 Xm3) isolates are single polar flagellate. They occur singly or in short chains. Certain variations in the cell size of Xml, Xm2 and Xm3 were observed but further studies are needed to confirm these observations. All the isolates are Gram-negative and non-capsulated. Pigmentation was less in the isolates Xml, Xm2 and Xm3 as compared to that of the parent isolate.

Biochemical properties: The results obtained on the biochemical properties of four isolates of *X. malvacearum* are presented in Table 5.

None of the isolates under study are capable of producing either ammonia or indole. All the isolates were found to liquefy gelatin and to hydrolyse starch, Xm2 was capable of hydrolysing more of starch than the other three isolates. H2 S was found to be produced by all the isolates but Xm2 was comparatively more active. Except Xm3 all the three were lipolytically active. The parent isolate and Xml gave positive V. P. test while Xm2 and Xm3 gave negative results. Except Xml the other three isolates gave positive M. R. test. None of the isolates was capable of reducing nitrate.

All the four isolates were found to coagulate litmus milk and to reduce the litmus but slight variations were observed in the quantities of acid produced. None of the isolates was found to produce gas in the media.

Utilization of various carbon sources: The results obtained on the comparative studies on the utilization of various carbon sources by the four isolates of *X. malvacearum* are presented in Table 6.

The parent isolate was found capable of utilizing all the carbon sources tested and it has produced acid in all the sources except in rhamnose, xylose and maltose. Comparatively Xml was a fast grower in xylose, fructose, rhamnose, levulose and maltose. Xm2 was a fast grower in sorbitol, glucose, galactose and rhamnose and produced more acid in all the sources except in xylose, rhamnose, levulose and maltose. The rate of growth of Xm3 was more in sorbitol, xylose and rhamnose and produced more acid in all the sources except in xylose, rhamnose, levulose and maltose.

Utilization of various Nitrogen sources: The results obtained on the comparative studies on the utilization of various nitrogen sources by the four isolates are presented in Table 7.

All the isolates utilized all the nitrogen sources tested. The parent isolate was a fast grower in arginine, histidine and glutamic acid. Xml was a fast grower in valine, leucin, glutamic acid and arginine. The rate of growth of Xm2 was more in glutamic acid, arginine, histidine and ammonium sulphate. Xm3 was found to grow fast in creatinum and in all the three inorganic nitrogen sources tried.

Comparative virulence : Actively growing isolates of Xm, Xml, Xm2 and Xm3 were inoculated on the healthy tender leaves of one month old cotton plants according to the procedure detailed under Materials and Methods. The results are presented in Table 8.

The results indicate that all the four isolates are equally pathogenic and no significant variation in their virulence was observed.

Wherever positive infections were obtained the pathogens were reisolated and compared with those of the respective original isolates and were found to be identical.

DISCUSSION :

The streptomycin resistant isolates of both the organisms were found to be identical with the parent isolates in their shape, Gram reaction and in possession of single polar flagellum. However, there were significant variation in their cell size and in some cases they were two to three times longer than the parent cells. Morphological variations such as pleomorphism, filament formation and enlarged cells in antibiotic-resistant cultures were reported by Gardner (1940), Fisher (1946), Stubblefield (1947) and Price *et al* (1947). Such changes are mainly attributed to the failure of fission. On the contrary Miller and Bohnhoff (1946) and Klimek *et al* (1948) have failed to observe any marked change in the shape and physiological behaviour in streptomycin-resistant cultures. The changes observed in the intensity of pigmentation in all the resistant isolates appears to be in confirmation with the results of Graessle *et al* (1946) and Seligmann and Wassermann (1947).

In the biochemical tests it was observed that the isolates were behaving much closer to the parent isolates except for a few changes, which might be due to a change in their metabolic pathways, involving enzyme mechanisms. The results on the comparative virulence of the isolates of both *X. citri* and *X. malvacearum* indicate no significant variation over those of respective parent isolates, which is in confirmation with the report of Rangaswami (1957).

SUMMARY :

Strains of *X. citri* and *X. malvacearum* resistant to streptomycin sulphate at 2500 $^{m}\mu/ml$, 3000 $^{m}\mu/ml$ and 4000 $^{m}\mu/ml$ were isolated by repeatedly sub culturing in nutrient broth with increasing concentrations of the antibiotic. The cells of the resistant strains were found to be relatively longer than the parent. The isolates were comparatively more active in the utilization of various carbon sources but there was no significant difference in the utilization of nitrogen sources excepting that the complex amino acids were better utilized by the resistant isolates than the parent isolates. The resistant strains of the two pathogenic species were found to be as infective as the respective parent isolates there being no apparent change in their virulence due to the development of resistance to streptomycin.

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TABLE 1

Comparison of Biochemical properties of four isolates of *Xanthomonas citri*

Isolate	NH_3 production	H_2S production	V. P. test	Methyl red	Lipolytic	Hydrolysis of starch	Gelatin	Indole	Litmus milk	Reduction of nitrate
Xc Parent	−	+	+	+	+	+	Liquified	−	Coagulated slight acid; no gas; litmus reduced	Nitrate not reduced
Xc−1	−	+	+	−	+	+	Liquified	−	Coagulated more acid; no gas; litmus reduced	Nitrate reduced
Xc−2	−	++	−	+	+	++	Liquified	−	Coagulated slight acid; no gas; litmus reduced	Nitrate in the presence of nitrite
Xc−3	−	+	−	+	+	+	Liquified	−	Coagulated; slight acid; no gas; litmus reduced	Nitrate in the presence of nitrite

TABLE 2

Utilization of various Carbon sources by the four isolates of *Xanthomonas citri*

Isolate		Glucose	Fructose	Galactose	Levulose	Xylose	Rhamnose	Lactose	Maltose	Sorbitol	Mannitol
Xc Parent	Growth	+	−	−	−	+	−	−	+	−	−
	Acid	−	−	−	−	−	−	−	−	−	−
	Gas	−	−	−	−	−	−	−	−	−	−
Xc−1	Growth	+	+	+	+	++	++	++	+	+	++
	Acid	+	+	+	++	+	−	++	−	+	+
	Gas	−	−	−	−	−	−	−	−	−	−
Xc−2	Growth	+	+	+	+	+	++	+	+	+	+
	Acid	+	+	+	+	+	−	+	−	+	+
	Gas	−	−	−	−	−	−	=	−	−	−
Xc−3	Growth	++	++	++	++	+++	+	+	++	+	+
	Acid	+	+	++	+	+	=	+	+	++	+
	Gas	−	−	−	−	−	=	−	−	−	−

TABLE 3

Utilization of various Nitrogen sources by the four isolates of *Xanthomonas citri*

Isolate	Ammonium sulphate	Sodium nitrite	Potassium nitrate	Creatine	Leucine	Glutamic acid	Arginine	Histidine	Valine	Trypto-phane
Xc Parent	+	+	+	+	−	+	+	+	+	+
Xc−1	+++	+	++++	++	++++	+	++++	+++	+	++++
Xc−2	+++	++	+++	++	+	++	+++	++++	++	+++
Xc−3	+	++	++	++	++	++	+++	+++	+	+++

TABLE — 4

Comparison of the virulence of four isolates of *X. citri* on citrus leaves

Isolate	Total number of leaves inoculated	Number of leaves infected				Final infection percentage.
		Number of days after inoculation				
		3	4	5	7	
Parents iolate	86	5	13	39	43	50
Xc — 1	64	7	18	21	31	49
Xc — 2	92	11	22	43	44	48
Xc — 3	104	13	21	47	49	47

TABLE 5

Comparison of biochemical properties of four isolates of *X. malvacearum*

Isolate	NH_3 production	H_2S production	V. P. test	Methyl red	Lipolytic	Hydrolysis of starch	Gelatin	Indole	Litmus milk	Reduction of nitrate
Xm Parent	−	+	+	+	S	+	Liquified	−	Coagulated; slight acid; no gas; litmus reduced	Nitrite not produced
Xm−1	−	+	+	−	S	+	Liquified	−	Coagulated; more acid; no gas; litmus reduced	Nitrite not produced
Xm−2	−	+++	=	S	S	++	Liquified	−	Coagulated; acid; no gas; litmus reduced	Nitrite not produced
Xm−3	−	+	−	+	=	+	Liquified	−	Coagulated; more acid; no gas; litmus reduced	Nitrite not produced

TABLE 6

Utilization of various Carbon sources by the four isolates of *X. malvacearum*

Isolate		Glucose	Fructose	Galactose	Levulose	Xylose	Rhamnose	Lactose	Maltose	Sorbitol	Mannitol
Xm Parent	Growth	++	++	++	+	++++	++++	+++	+++	+++	+
	Acid	++	++	++	+	−	−	+++	−	++	++
	Gas	−	−	−	−	−	−	−	−	−	−
Xm−1	Growth	+	++	+	++	+++	++	+	+	+	+
	Acid	+	++	+	−	+	−	+	−	+	+
	Gas	−	−	−	−	−	−	−	−	−	−
Xm−2	Growth	++	+	++	+	+	++	+	+	+++	+
	Acid	++	++	++	−	−	−	+	−	++	+
	Gas	−	−	−	−	−	−	−	−	−	−
Xm−3	Growth	+	+	+	++	++	+++	+	++	++	+
	Acid	+	+++	+	+++	+	−	+	−	++	+
	Gas	−	−	−	−	−	−	−	−	−	−

TABLE 7

Utilization of various Nitrogen sources by the four isolates of *X. malvacearum*

Isolate	Ammonium sulphate	Sodium nitrite	Potassium nitrate	Creatine	Leucine	Glutamic acid	Arginine	Histidine	Valine	Trypto-phane
Xm Parent	+	+	+	+	+	++	++++	+++	+	+
Xm−1	+	+	+	++	++	+++	+++	+	++	++
Xm−2	++	+	+	+	+	++++	++	++	+	+
Xm−3	++	++	++	+++	+	+	+	+	+	+

TABLE — 8

Comparison of the virulence of four isolates of *X. malvacearum* on cotton leaves

Isolate	Total number of leaves inoculated	Number of leaves infected				Final infection percentage.
		Number of days after inoculation				
		3	4	5	7	
Parent isolate	80	4	16	37	40	50
Xm — 1	104	6	23	40	53	51
Xm — 2	110	3	19	45	57	52
Xm — 3	96	7	28	49	50	52

A COMPARISON OF THE HYDROCYANIC ACID CONTENT OF THE LEAVES AND STEMS OF SEED AND RATOON PLANTS OF SIX STRAINS OF SORGHUM

by

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It is well known that sorghum crop (*Sorghum vulgare* pers.) constitutes staple food for cattle population in India. It contains a cyanogenetic glucoside, 'dhurrin' which could release hydrocyanic acid (HCN), which is toxic to the animals, sometimes proving fatal to the cattle consuming it. In India sorghum poisoning has been noted as early as in the last quarter of nineteenth century (Pease 1897). Acharya (1933) investigated somewhat elaborately the development of prussic acid in sorghum. Lakke Gowda (1955) brought out the variations in HCN contents of four different varieties of sorghum grown in Mysore State. Mahudeswaran *et al* (1958) studied the variations in HCN content of the shoots of five strains of sorghum viz., Co. 10, Co. 11, K. 1, K. 3 and A. S. 8208, grown in Madras State. No studies have been made so far to compare the HCN concentrations in the seed and ratoon plants of sorghum strains. In this paper results on the studies made to compare the HCN content in the leaves and stems, of seed and ratoon plants at various stages of growth of six strains of sorghum are reported.

MATERIAL AND METHODS

The following six sorghum strains commonly grown in Madras State were selected for these studies. The local names of the strains are given in parenthesis. Co. 5 (*Chinnamanjal cholam*); Co.1 (*Periyamanjal cholam*); Co.4 (*Sencholam*); Co.19 (*Thalaivirichan cholam*); K.1 (*Irungu cholam*): and K.3 (hybrid of *Periyamanjal* and *Irungu cholam*).

Healthy seeds of the sorghum strains were sown in cement-pots, 24"x 12"x 9", filled with well-sieved garden soil. Each strain was sown in 4 pots at 12 seeds per pot, giving equal spacing. Watering was done every alternate day and the pots were kept in the green house till the experiment was completed. When required, one plant from each of the four pots was pulled out with the root system intact, thus collecting 4 plants in each strain for estimating HCN. The plants were pulled out invariably during 1 to 2 p. m. on the sampling date. The stem and leaves were cut separately from each plant and were bagged in separate polythene bags. They were then kept in a refrigerator for 24 hours for freezing.

The freezed samples were cut into small bits with a laboratory feed-chopper and mixed thoroughly before collecting samples for estimating HCN. The method followed for estimating the HCN was similar to the ones recommended by Hogg and Ahlgren (1942) and Trione (1960) but after conducting several preliminary estimations, some modifications were made. The procedure is briefly described below: The freezed samples were cut into small bits, mixed thoroughly and 0.25 g of representative sample weighed out in a test tube. 0.5 ml chloroform was added to the sample and the test tube closed with a cork, suspending a strip of filter paper which was previously soaked in alkaline sodium picrate solution. The tube was incubated at room temperature for 24 hours during which period the HCN evolved from the plant tissue turned the sodium picrate in the filter paper into reddish sodium picramate. The substance was then transferred into clean distilled water (10 ml) and the intensity of the colour compared using Hellige's colour comparator. On the basis of colour intensity the HCN concentration was calculated and expressed as mg of HCN/100 g of plant tissue on dry weight basis. The HCN contents were estimated at 15 day intervals both in the 'seed crop' and 'ratoon crop', the plants having been ratooned after the maturity of grains in the first formed earheads.

EXPERIMENTAL RESULTS

1. *HCN content of leaves* :— Comparative data on the HCN content of leaves of the six sorghum strains are presented in Table I.

Except strain K.1 the other five strains of sorghum contained initial high concentrations of HCN in the leaf which got gradually reduced with the plant growth. In K.1 there was high concentration of HCN upto 45 days, after which it got reduced. HCN was found in Co.1 and Co.4 throughout the growing period, whereas in Co.5 and Co.19 there was no HCN in the leaves on the 45th and 60th days. In K.1 and K.3 there was no HCN in the leaves just prior to harvest.

Unlike in the seed crop the maximum HCN content in the leaves of ratoon crop was recorded in the strains Co.5, K.1, Co.19 and K.3 in about 30 to 60 days, whereas in Co.1 and Co.4 the maximum concentration was on the 15th day. In the leaves of ratoon plants of K.1, K.3, Co.1 and Co.4 there were more concentrations of HCN than in the seed plants, whereas in Co.5 and Co.19, the HCN contents of the leaves of ratoon plants were lesser than the respective seed plants.

2. *HCN content of stems* :— The comparative data on the HCN content of stems of the six sorghum strains are given in table II.

The HCN content in all the strains was high in the initial stages but there was gradual decrease after 15 days, extending upto the time the plants were ready for harvest. In Co.19, some fluctuations in the HCN content were noted when the plants were about 75 to 105 days old. The maximum of 130 mg of HCN/100 g of stem(dry tissue) was recorded in Co.5 on the 15th day and the minimum of 2 mg of HCN was recorded in K.3 on the 120th day. In general, the minimum HCN in the stem was recorded in all the sorghum strains during the earhead stage.

The stems of ratoon plants contained relatively more HCN than the stems of seed plants of the same sorghum strain. The maximum concentration of 225 mg of HCN/100 g of stem was recorded in Co.4. This concentration is almost double that recorded in the stems of the strain when raised through seed. In Co.1 the maximum concentration was 200 mg which is nearly thrice that in the stem of seed plants of the same strain. In Co. 1, Co. 4, Co. 5 and Co. 19 there was an initial high concentration of HCN in the stem, which gradually decreased reaching a very low concentration at the times of flowering and maturity. In K.1 and K.3 there was an increase in the HCN content of the stem during the initial periods i.e, in about 15 to 30 days after the first crop was ratooned. This initial increase soon got reduced, reaching low concentrations after flowering.

DISCUSSION

The above results indicate that the HCN content of sorghum leaf was high in the initial stages which got reduced with plant growth. This is in agreement with the findings of earlier workers (Willaman and West 1915, Ghose 1919, Swanson 1921, Acharya 1933). In all the six sorghum strains the HCN content in stem was more than that of the leaf. The earlier workers (*loc. cite*) have found the stem to contain less HCN than the leaf but these variations might be because they expressed the HCN content on fresh weight basis of the plant tissues. Acharya (1933) found that the HCN contents of leaves, stem and roots were in the proportion 3 : 1 : 7 on fresh weight basis. The analysis of moisture percentage of leaf, stem and root showed about 3 times more of moisture in the stem than that of leaf, but the moisture contents of both leaf and root were about the same throughout. Considering this factor, it could be seen that the results obtained by the earlier workers are not much different from the results in the present studies. The results reported by Mahudeswaran *et al* (1958) on the HCN content of the strains K. 1 and K. 3 are in general agreement with the results

obtained in this study. In general, the ratoon crop contained more HCN in the leaf and stem than the seed crop, which agrees with the previous reports (Willaman and West 1915, Hogg and Ahlgren 1943, Ambastha and Jha 1955).

The theory of formation of HCN in sorghum plant is still controversial, as different views prevail among the scientists (Dunstan and Henry 1902, Willaman and West 1916, Willaman 1917, Rosenthaler 1927, Stekelenburg 1931, Acharya 1933, Frey-Wyssling 1942, Franzke 1948). According to Acharya (1933) the HCN has a close relationship with the accumulation of starch in the plant and all plants rich in HCN, like young cholam seedlings, plants stunted due to drought, ratoons and secondary shoots are also rich in starch. But Briese and Couch (1938) reported that there was no correlation between the quantity of starch and HCN in sorghum. The results obtained in the present studies also lend support to the latter view. More HCN was found to be present in the stem than in the leaf throughout the growth period in seed crop as well as ratoon crop. But HCN was not found in the leaves at certain stages of growth viz., from 45 to 60 days in Co. 5 and Co. 19 and after 120 days in K. 1 and K. 3 strains. Generally the leaves contained more of starch than the stem during these stages of plant growth (Barbera and Fazio 1940, Akazawa *et al.* 1960). Further detailed studies on the metabolic pathways and their relation to HCN and starch content of sorghum plants at different stages of growth would help in understanding this complicated problem.

SUMMARY

The HCN content of leaf and stem of sorghum strains Co. 1, Co. 4, Co. 5 Co. 19, K. 1 and K. 3 were estimated both in the seed plants and ratoon plants at different stages of development. All the six strains contained high concentrations of HCN in the leaf and stem in the seedling stages, which got reduced with age. The peak period of the concentration of HCN in the plant parts varied with the strain. In some strains the ratoon plant contained more HCN in the leaf and/or stem.

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TABLE I

HCN–Content of sorghum leaf

(in mg/100 g of tissue on dry weight basis)

Sorghum strain	Age of plant in days													
	15	30	45	60	75	90	105	120	135	150	165	180	195	210
Co.5	75	8	0	0	11	8	4	17	11	22	3†	—	48	56
Co.1	63	20	7	25	7†	75	25	25	17	13	—	—	—	—
Co.4	75	8	10	4	19†	83	33	33	24	—	—	—	—	—
K.1	31	21	33	12	17	28	13	0†	—	20	25	38	26	5
Co.19	38	17	0	0	4	13	20	3	3	33	6†	—	52	32
K.3	38	14	8	0	4	3	8	0†	—	48	23	16	15	7

† Plants harvested and allowed to ratoon

TABLE II

HCN-content of sorghum stem

(mg/100 g of tissue on dry weight basis)

Sorghum strain	Age of plant in days													
	15	30	45	60	75	90	105	120	135	150	165	180	195	210
Co. 5	133	43	40	33	23	40	22	40	36	21	9†	—	154	98
Co. 1	67	33	60	30	20†	200	66	33	46	37	—	—	—	—
Co. 4	110	33	23	20	10†	225	66	33	20	—	—	—	—	—
K. 1	125	74	58	44	22	46	86	5†	—	78	154	54	22	15
Co. 19	100	38	33	25	30	43	66	22	18	29	18†	—	124	64
K. 3	125	50	38	33	33	14	29	2†	—	96	164	60	36	24

† Plants harvested and allowed to ratoon

OBSERVATIONS ON THE INFLUENCE OF SOUND WAVES ON THE GROWTH VIGOUR AND REPRODUCTIVE PHASE IN *URGINEA INDICA* KUNTH

by

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Annamalai University

(Communicated by Professor T. C. N. Singh, D. Sc., Annamalai University)

INTRODUCTION

Previous reports in this laboratory have shown that sound waves produced by tuning fork have the effect of increasing the rate of vital processes of plants, such as carbon assimilation, respiration and transpiration (1, 2, 3). The present work pertains to the growth and reproduction in *Urginea indica* Kunth, the Indian Squill, in relation to excitation by sound waves produced by tuning fork.

MATERIAL AND METHOD

For this purpose, bulbs of Indian squill were planted in a plot of ground in concentric circles in the centre of which, an electrically-run tuning fork (of 100 frequency) was placed. The tuning fork was switched on for 30 minutes every day at 6 A. M. The bulbs were so disposed that no bulb was more than 3 feet, distant from the tuning fork. Another plot was chosen far away from the previous one where also, bulbs of *Urginea* were planted. Care was taken to see that the size and number of bulbs and the pattern of planting as also the nature of the soil were identical in both the plots.

OBSERVATIONS

Growth measurements of the shoot system were made after 12 months of sound treatment. The results obtained are interesting and are recorded in the following table (Table-1)

TABLE — I

Serial No. of plants.	Length of shoot		$\frac{E-C}{C} \times 100$
	Control	Experimental	
1	4.5 cm.	6.0 cm.	33.3
2	5.0 cm.	7.5 cm.	50.0
3	5.5 cm.	7.5 cm.	36.3
4	7.0 cm.	8.0 cm.	14.2
5	7.0 cm.	8.5 cm.	21.4
6	7.5 cm.	9.5 cm.	26.6
7	9.0 cm.	14.5 cm.	61.1
8	9.5 cm.	14.5 cm.	55.5
9	10.0 cm.	15.0 cm.	50.0
10	10.5 cm.	15.0 cm.	42.3
11	11.0 cm.	15.0 cm.	36.4
12	11.5 cm.	15.0 cm.	30.4
13	13.0 cm.	19.0 cm.	46.2
14	13.0 cm.	19.0 cm.	46.2
15	13.5 cm.	19.0 cm.	40.7
16	13.5 cm.	19.0 cm.	40.7
17	14.0 cm.	19.5 cm.	39.3
18	14.5 cm.	19.5 cm.	34.5
19	15·0 cm.	20.0 cm.	33.3
20	15.5 cm.	20.5 cm.	32.3
21	16.0 cm.	20.5 cm.	28.1
22	16.5 cm.	20.5 cm.	24.2
23	17.0 cm.	21.0 cm.	23.5
24	17.5 cm.	21.5 cm.	22.8
25	18.0 cm.	23.5 cm.	30.5

Serial No. of plants	Length of shoot		$\frac{E-C}{C} \times 100$
	Control	Experimental	
26	18.5 cm.	24.5 cm.	32.4
27	19.0 cm.	24.5 cm.	28.9
28	19.5 cm.	24.5 cm.	25.7
29	20.0 cm.	24.5 cm.	22.5
30	20.0 cm.	26.0 cm.	30.0
31	20.5 cm.	26.5 cm.	29.2
32	20.5 cm.	26.5 cm.	29.2
33	21.0 cm.	27.0 cm.	28.6
34	21.0 cm.	27.0 cm.	28.6
35	21.5 cm.	28.5 cm.	32.5
36	21.5 cm.	28.5 cm.	32.5
37	21.5 cm.	28.5 cm.	32.5
38	22.0 cm.	30.5 cm.	38.6
39	22.0 cm.	31.5 cm.	43.2
40	22.5 cm.	31.5 cm.	40.0
Total			$\frac{1374.2}{40} = 34.4$

From a perusal of the table it will be seen that the sound excited plants have registered much greater growth than the corresponding controls. On the average the experimental plants have an increase in growth value to the extent of 34% over the control.

Besides the foregoing observations on the growth vigour, another notable behaviour on the part of the sound-treated *Urginea* was that it flowered much earlier than the control. Actually while in the experimental plot some of the bulbs had put forth the flowering scapes 7 months after planting, those of the control plot were still in the vegetative stage and only in the 8th month after planting, some signs of appearance of flowering scapes could be seen. Furthermore, as contrasted with the control, the number of flowering scapes in the experimental plot were 40% in excess over that of the control. All these facts have been entered in the following table.

TABLE—2

Plot No.	Date on which the bulbs were planted.	Date on which the flower scapes appeared	Time taken for flowering	Total No. of flower scapes produced
1. Control	28—8—1961	18—4—1962	8 months	25
2. Exptl.	28—8—1961	7—3—1962	7 months	35

DISCUSSION

The foregoing observations make it abundantly clear, that sound waves produced by tuning fork exercise an appreciable influence on the growth rate of *Urginea*. It has been already shown by previous workers in the Annamalai School of Botany, that sound waves have the effect of augmenting the rates of vital processes of plants like carban assimilation, respiration and transpiration. It is therefore, quite intelligible that the enhanced rates of vital processes ultimately lead to more vigorous growth and earlier flowering in the sound treated plants. This is precisely what has happened in the case of the experimental *Urginea* as compared with the control.

SUMMARY

Previous reports in this laboratory have shown that sound waves impinging on the leaves bring about considerable increase in the stomatal frequency which as a consequence leads to increased rates of vital processes of plants like carbon assimilation, respiration and transpiration. The present work pertains to observations on the growth values of the Indian Squill, *Urginea indica* Kunth. as influenced by sound waves from an electrically-run tuning fork. Herein, have been recorded growth measurements of sound treated *Urginea* plants and their corresponding controls after both have grown for 12 months. The experimental plants have registered an increase of growth value by 34% over the controls. Furthermore, the increased growth vigour appears to have hastened flowering in the experimentals with the result that the sound treated plants put forth flowering scapes one month earlier than the controls. Thus it will be clear that the increased rates of vital processes brought about by the influence of sound waves ultimately lead to an increase in growth vigour and earlier flowering.

ACKNOWLEDGMENT

It gives me much pleasure to express my grateful thanks to Prof. T.C.N. Singh, D.Sc.,D.Ph.,F.B.S.,P.L., Professor and Head of the Department of Botany, Annamalai University for his kind encouragement and critical suggestions in the conduct of the experiments. I am thankful also to the members of the Botany Department Research Club for their helpful criticisms.

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PRELIMINARY STUDIES ON THE EFFECTS OF ULTRAVIOLET RAYS ON THE CHROMOSOMES OF *URGINEA INDICA*, KUNTH. (THE INDIAN SQUILL)

By

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INTRODUCTION

For some time in the recent past, work on the physiological response of a variety of tuberous plants like *Colocasia antiquorum*, Schott. to irradiation with ultraviolet rays has been in progress (Singh and Pannirselvam, 1955). The present work was undertaken on the suggestion of Professor Singh, Head of the Department of Botany, Annamalai University, in order to find out how far ultraviolet irradiation brings about alterations in the chromosomes of the common Indian Squill, *Urginea indica*, Kunth. Since the discovery by Muller (1927) quoted by Mc Quate (1954) that gene mutations could be induced in Drosophila by the administration of X-rays, a number of investigators have shown that ultraviolet irradiation is also capable of causing mutations in the gene (Stadler, 1938; Stadler and Uber, 1942; Faberge, 1951; and Stadler and Swanson, quoted by Emmerling, 1955). But all these investigations pertained to the effects of ultraviolet on the pollen tissue and consequently on the meiotic behaviour of the chromosomes. However, comparatively small amount of work seems to have been done so far on the effect of ultraviolet on the mitotic chromosomes of root tips (Mather and Stone, 1933). In the present undertaking the root tips of *Urginea indica*, Kunth were subjected to the ultraviolet irradiation and the behaviour of the somatic chromosomes has been studied.

MATERIALS AND METHODS

All irradiation was carried out in a dark room, the source of ultraviolet being a Hanovia Fluorescence Lamp, Model XI made by Hanovia Ltd., London with an energy intensity being less than 3900 Angstrom units. Bulbs of

Urginea were grown in bottles containing tap water and when fresh root tips had emerged, the bulbs were irradiated in the moist condition with ultraviolet. Duration of treatment as well as distance between the source of irradiation and the material was changed as indicated below:

DISTANCE		DURATION
9 inches	...	5 minutes
9 ,,	...	10 ,,
9 ,,	...	15 ,,
18 ,,	...	5 ,,
18 ,,	...	10 ,,
18 ,,	...	15 ,,
18 ,,	...	30 ,,
18 ,,	...	1 Hour
18 ,,	...	2 Hours
24 ,,	...	5 minutes
24 ,,	...	10 minutes
24 ,,	...	15 minutes

For studying the behaviour of the somatic chromosomes, permanent root tip squashes stained in aceto-carmine were prepared according to the 'Rapid Acetocarmine Squash Technique' devised in this laboratory (Rangaswami, 1956). Paraffin sections were also cut 12 microns thick and stained in Heidenhain's iron-alum haematoxylin.

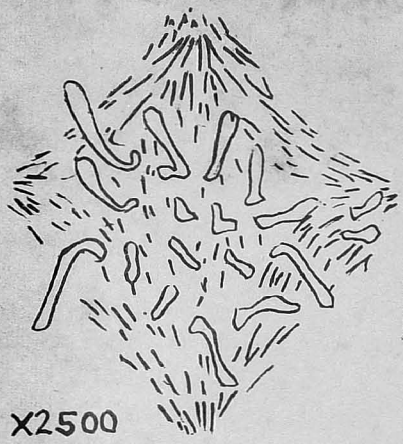
OBSERVATIONS

Appreciable chromosomal changes could be recognised under treatment of 18″ distance and 2 hours′ duration. The immediate effect of ultraviolet was to inhibit the mitotic division so that cells examined soon after irradiation contained mostly resting nuclei. But when cells were examined 24 hours after the treatment, they showed abmormalities of nuclear division. In the first place, in a few cells, the number of chromosomes have apparently increased. This is presumably due to the inhibiton of the spindle mechanism which has arrested the normal anaphasic movement of the chromatids towards the poles. The result is that the longitudinally split chromosomes (chromatids) lie scattered about the equator of the cell (Fig. 1.)

Secondly, fragmentation of the chromosomes has taken place. In most cases, there were formed distal fragments. The behaviour of these distal fragments affords an interesting comparison with the behaviour of univalents in the meiosis of sterile hybrids. Just as in the latter, here also, due to the lack of normal disjunction, these fragments lag here and there within the cell. But unlike univalents which at least in the second meiotic division usually undergo splitting and manage to reach the poles, these laggards get lost in the cell. This is inferred from two evidences namely, the positive presence of lagging fragments in some cells during post-metaphasic and anaphasic stages (Fig. 2 and 3), and from the occurrence of shortened chromosomes in the place of the usually long ones. These distal fragments are lost during division evidently for want of centromeres.

Another striking chromosomal abnormality was observed in a few cells. Figure 4, shows an anaphase stage of nuclear division where two chromatin bridges are seen. Such chromatin extensions could happen only when these chromatids have come to possess two attachment constrictions, which themselves could have come about by fragmentation and subsequent end-to-end fusion of two proximal fragments each having its attchment constriction. In certain cases the anaphasic pull seems to have exercised too much strain on the longdrawn out chromatids with the result, they have got broken in the middle (Fig. 5.)

Peculiarly enough, in a few cases alongside the formation of such long-drawn out chromatids, the configuration of the impaired spindle has undergone a curvature which fact is evidenced, by the curved nature of these chromatids (Fig.6.)

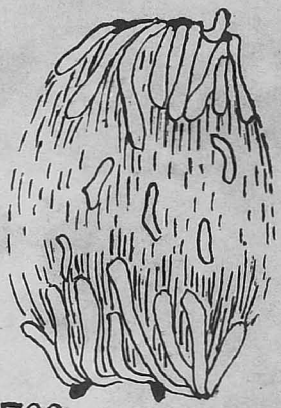


X2500

1

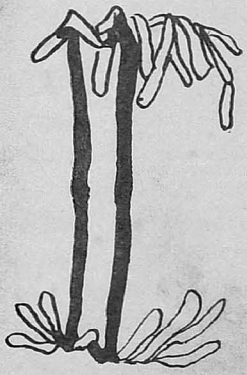
2

X3800



X2500

3

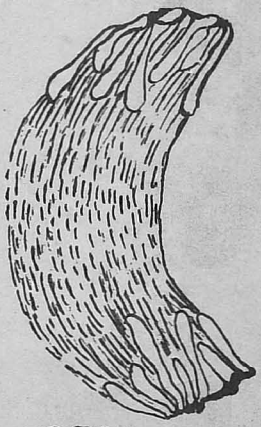


X2500

4

X4500

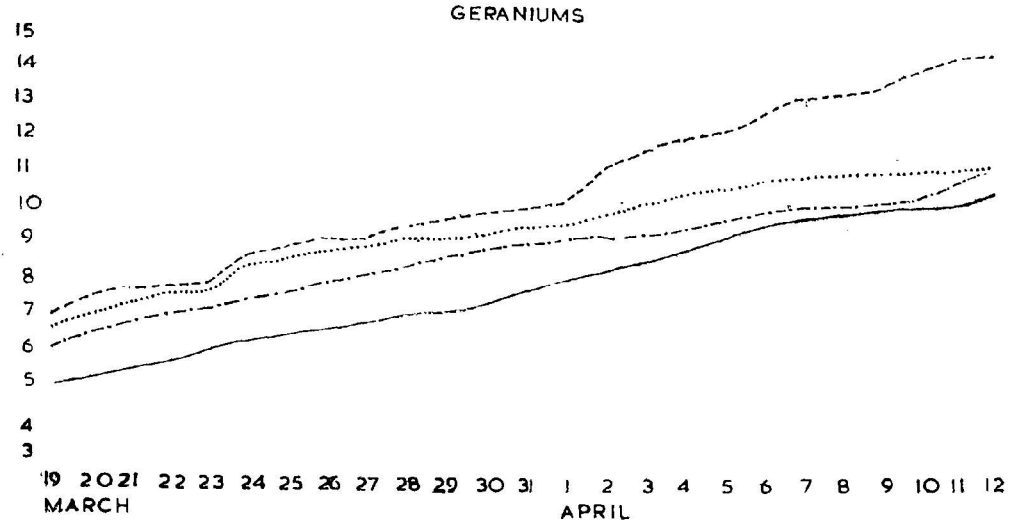
5



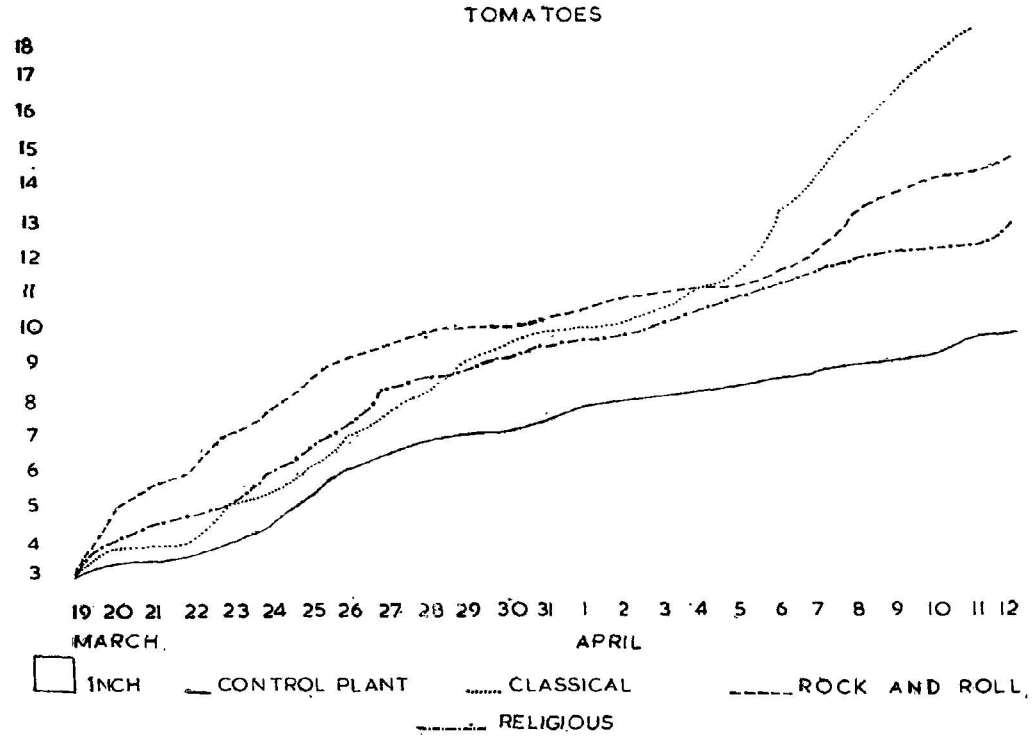
X2500

6

Graph I



Graph II



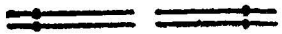
Graphs I and II ; Showing growth in length of the experimental plants of Tomato and Geranium under the irradiation of musical sounds Classical, Rock & Roll and Religious Music as compared to the control plants.

DISCUSSION

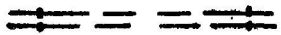
The peculiar behaviour of the distal fragments which are formed by the influence of ultraviolet rays has already been indicated in the text. As they happen to be accentric, their movement is haphazard and they do not survive at the end of the mitotic division. Presumably they get lost during mitosis and the sequel is that at the next metaphase some of the normally long chromosomes become comparatively shorter. It is, therefore, clear that unless a chromosome or its fragment possesses an attachment constriction, it cannot become part of the permanent hereditary complement of the nucleus.

The occasional formation of chromatin bridges during anaphase is evidently due to the dicentric nature of the chromatids involved therein. As pointed out earlier, such dicentric chromatids must have been derived ds products of fusion between two proximal fragments each possessing its attachment constriction. Since each chromosome undergoes longitudinal division before the anaphasic separation, we usually find two chromatid bridges. The lengths of these abnormal chromatids have been found to be equal. This fact seems to afford an indirect clue as to the time of splitting of the chromosomes. Whether or not the splitting takes place before the resting stage of the nucleus can be examined in the light of the present finding. Assuming that the splitting has taken place in the previous telophase prior to the commencement of mitosis, the chromosomes will have already become double strands even from the resting stage onwards. In that case, the fragmentation due to ultraviolet rays is not likely to occur to the same extent in the two distinct strands of any given chromosomes Naturally, further random recombination of these fragments will result in unequally long chromatid bridges. No such unequal chromatid bridges have been observed here. It seems, therefore, safe to assume that at the time of the influence of ultraviolet rays, during the resting stage and prior to the prophase each chromosome must have behaved as a unitary structure and it is only after the abnormality is caused by the ultraviolet rays, that the chromosomes must have undergone division resulting in two equally long chromatid bridges (Darlington, 1931; 1932), Irradiation experiments with X-rays on *Crocus* species have led to a similar conclusion (Mather and Stone 1933). The following diagrammatic scheme illustrates this point:

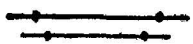
Resting stage with the chromosome already longitudinally split before U. V. influence



U. V. influence resulting in unequally abnormal chromatids of unequal lengths



End-to-end fusion of proxima fragments to form dicentric chromatids of unequal lengths.



Anaphase showing unequally long chromatid bridges

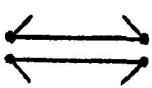
Resting stage wite the chromosome as a unitary structure

Fragmentation due to U. V. influence

Longitudinal splitting of the chromosome after U. V. resulting in equally abnormal chromatids

End-to-end fusion of proximal fragments to form dicentric chromatids of equal lengths.

Anaphase showing equally long chromatid bridges



Fragmentation and fusion of chromosomes have been considered to be important factors in chromosome evolution. The number and morphology of the chromosomes of different species of *Crocus* are supposed to have arisen by the operation of these processes. Normally chromosome evolution has proceeded on the lines of duplication of the entire complement (euploidy) or part of it (aneuploidy) with the subsequent attainment of secondary balance. But in quite a few cases as in *Carex* (Heilborn, 1924), *Cardamine* (Lawrence, 1931 b), *Crocus* (Mather, 1932), *Nicotiana* (Vilmorin and Simonent, 1928 quoted by Mather and Stone, 1933) and *Crepis* (Navashin, 1932 quoted by Mather and Stone, 1933), fragmentation and fusion also seem to have contributed to appreciable chromosomal alterations that have become part of the hereditary make up.

SUMMARY

Previous work in this laboratory has shown that irradiation of the tubers of *Colocasia antiquorum*, Schott. with ultraviolet rays brings about appreciable physiological reaction in the shape of larger size, higher yield and increased growth vigour in the succeeding generations. The present investigation was undertaken with a view to study the possible influence of ultraviolet rays upon the mitotic chromosomes of the common Indian Squill, *Urginea Indica*, Kunth.

Some abnormalities in the mitotic division have been observed. The chromosomes after their longitudinal splitting become promiscuously distributed within the cell, presumably due to the impaired spindle mechanism.

Fragments are formed some of which being distal and accentric lag for some time like univalents in the meiosis of sterile hybrids and ultimately get disorganised at the close of mitosis. Consequently, the normally long chromosomes appear to have become shorter in the succeeding metaphase.

More rarely the proximal fragments with attachment constrictions give rise, by end to end fusion, to dicentric chromosomes which naturally become stretched to form chromatin bridges during anaphase.

In the light of the observations made here as to the nature of the chromatin bridges, evidence has been adduced that the chromosomes undergo longitudinal splitting during the metabolic condition of the nucleus after the influence of ultra-violet irradiation and not in the previous telophase prior to mitosis.

The significance of fragmentation and fusion of chromosomes as contributing to chromosomal evolution in plants has been indicated. Normally chromosome evolution has proceeded on the lines of duplication of the entire complement (euploidy) or part of it (aneuploidy) with the subsequent attainment of secondary balance. But the present work suggests that chromosomal fragmentation and fusion may also help to bring about alterations of a more or less permanent character in the hereditary make up of plants.

ACKNOWLEDGMENT

It is a source of immense pleasure to express my grateful thanks to Professor T. C. N Singh, M.Sc., D.Sc., F.B.S., Professor & Head, Department of Botany for suggesting the problem and for his continued encouragement, valuable suggestion and criticisms from time to time. I am also much obliged to the members of the Botany Department Research Club for their helpful discussion on the topic during the weekly meetings of the Club.

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SOME RECENT DEVELOPMENT IN DESIGN OF EXPERIMENTS

SRI M. C. CHAKRABARTI

BALANCED INCOMPLETE BLOCK DESIGNS

1. *Introduction.* A balanced incomplete block design (BIBD) with parameters (v, b, r, k, λ) is an arrangement of v objects or treatments into b sets or blocks such that (*i*) each set contains $k<v$ different treatments (*ii*) each treatment occurs in r different blocks and (*iii*) each pair of treatments occurs together in λ blocks. Essentially the construction of such a design is equivalent to the filling up of a $v \times b$ matrix N with 0 and 1 such that every row sum is r. every column sum is k and $NN' = (r-\lambda)\, I_v + \lambda\, E_{vv}$ where I_p is the identity matrix of order p and E_{pq} is a $p \times q$ matrix all of whose elements are unity. The sum total of all the elements of N on the one hand is bk and on the other vr. Again, the sum total of all the elements in NN' is on the one hand $vr + \lambda\, v(v-1)$ and on the other $bk^2 = vrk$. Hence

$$bk = vr \tag{1·1}$$

$$\lambda\,(v-1) = r(k-1) \tag{1·2}$$

Let the first row of $N'N$ be $(k, l_1, \ldots, l_{b-1})$. Then leading terms of $N'NE_{b1}$ and $(N'N)^2$ are respectively $k + l_1 + \ldots + l_{b-1}$ and $k^2 + l_1^2 + \ldots + l^2_{b-1}$, Direct calculations give these as rk and $(r-\lambda)\,k + \lambda\, k^2$ respectively. Hence

$$l_1 + l_2 + \ldots + l_{b-1} = k\,(r-1) \tag{1·3}$$

$$l^2_1 + l^2_2 + \ldots + l^2_{b-1} = (r-\lambda)k + (\lambda-1)k^2 \tag{1·4}$$

Writing $\bar{l} = (l_1 + l_2 + \ldots + l_{b-1})/(b-1)$, we get

$$(b-1) \sum_{i=1}^{b-1} (l_i - \bar{l})^2 = k\,(v-k)\,(b-v)\,(r-\lambda)/v \tag{1·5}$$

As the other terms in the numerator of the fraction in (1·5) are positive we must have

$$b \geqslant v \tag{1·6}$$

Thus, though (1·1) and (1·2) are satisfied $v = 16$, $b = 8$, $r = 3$, $k = 6$, $\lambda = 1$ will not yield a BIBD as (1·6), is not satisfied. (1.1), (1·2) and (1·6) are necessary conditions for the existence of a BIBD.

A BIBD is said to be symmetrical when $b = v$. From (1·5) and (1·3), in the case of a symmetrical BIBD, between any two blocks there are λ treatments in common.

A BIBD is said to be resolvable if the blocks can be divided into r sets of n such that the blocks of a given set contain each treatment exactly once. In this case $v = nk$, $b = nr$ and

$$r - \lambda = rk - v\lambda = rk - nk\lambda = k(r - n\lambda) \qquad (1.7)$$

$\therefore \quad r - n\lambda - 1 \geqslant 0$ and

$$k(b - r) = (r - \lambda)(-1)v = k(r - n\lambda)(v - 1)$$

$$\therefore \quad b = v + r - 1 + (r - n\lambda - 1)(v - 1) \qquad (1.8)$$

Hence (i) $b \geqslant v + r - 1$ (ii) $k/(r - \lambda)$ and (iii) a symmetric BIBD can never be resolvable.

If in a resolvable BIBD, any two blocks of different sets have the same number of treatments, m, in common, the design is said to be affine resolvable. From (1.3) $mn(r - 1) = k(r - 1)$. Hence $k = mn$ in the case of an affine resolvable BIBD. Also $k^2 = mnk = mv$, $\therefore \; v/k^2$. From (1.4)

$$m^2n(r - 1) = k(r - \lambda) + (\lambda - 1)k^2 = k^2(r - n\lambda - 1 + \lambda) \text{ from } (1.7)$$

$$\therefore \quad m(r - 1) - mn\lambda = k(r - n\lambda - 1)$$
$$(k - m)(r - n\lambda - 1) = 0, \quad \therefore \; r = n\lambda + 1$$

Hence from (1.8), $b = v + r - 1$, and from (1·7), $r = k + \lambda$

$$nr = n^2m + r - 1$$

$$r = \frac{n^2m - 1}{n - 1}$$

$$\lambda = r - k = \frac{n^2m - 1}{n - 1} - mn = \frac{mn - 1}{n - 1} = m + \frac{m - 1}{n - 1}$$

$m - 1 = t(n - 1)$ where t is a non-negative integer

Hence $m = t(n - 1) + 1$

$$r = \frac{n^3 t\ (n-1) + n^2 - 1}{n - 1} = n^2 t + n + 1$$

$$\lambda = nt + 1, \qquad k = n\,[\,(n-1)\,t + 1\,]$$

$$v = n^2\,[\,t(n-1) + 1\,]$$

$$b = n(n^2 t + n + 1)$$

2. Impossibility of existence of BIBD with certain parameter sets

$(v,\ b,\ r,\ k,\ \lambda)$

Till the publication of Schutzenberger's paper in 1949 [1] the only method known to us about deciding the impossibility of a BIBD with a particular (v, b, r, k, λ) set was the method of exhaustive enumeration. Schutzenberger observed that $\det NN' = rk\,(r - \lambda)^{v-1}$ and in the case of symmetrical BIBD

$$\det N = (\det NN')^{\frac{1}{2}} = \pm\, r\,(r - \lambda)^{\frac{v-1}{2}}$$

Hence in a symmetrical BIBD with an even number of varieties $r - \lambda$ must be a perfect square. Thus, in particular a BIBD with any of the set of parameters (22, 22, 7, 7, 2), (46, 46, 10, 10, 2), (92, 92, 14, 14, 2), (106, 106, 15, 15, 2), (172, 172, 19, 19, 2) and (34, 34, 12, 12, 4) is impossible.

Shrikhande [2] made use of the deep Hasse-Minkowski criteria [3] for the rational equivalence of quadratic forms to prove the non-existence of certain symmetrical BIBD with an odd number of treatments. In the case of symmetrical BIBD, N is non-singular and by the rational n on-singular transformation $y = N'x$, $x'\,NN'x$ can be converted into $y'y$. Hence NN' and I_v are rationally equivalent. Now for every odd prime p

$$C_p(NN') = (-1, rk)_p \ (-1, r-\lambda)_p^{\frac{v(v-1)}{2}} \ (r-\lambda, rk)_p^{v-1} \ (v, rk)_p \ (v, r-\lambda)_p$$

In the case of symmetrical BIBD with odd v, for every odd prime

$$C_p(NN') = (-1, r-\lambda)_p^{v(v-1)/2} (v, r-\lambda)_p = C_p(I_v) = 1.$$

Hence the following designs, in particular, are impossible: (137, 137, 17, 17, 2), (67, 67, 12, 12, 2), (103, 103, 18, 18, 3), (53, 53, 13, 13, 3), (43, 43, 15, 15, 5), (77, 77, 20, 20, 5).

Connor [4] observed that if N is partitioned into $(N_t, \overline{N}_t)$ where N_t, $\overline{N}_t$ denote respectively the first t and last $b-t$ columns of N and if

$$N^* = \left[\begin{array}{c|c} N_t & \overline{N}_t \\ \hline I_t & 0 \end{array}\right] \qquad (1\cdot9)$$

Then $N^*N^{*\prime} = \left[\begin{array}{c|c} NN' & \overline{N}_t \\ \hline \overline{N}'_t & I_t \end{array}\right]$

$$\det N^*N^{*\prime} = kr^{1-t}(r-\lambda)^{v-1-t} \det C_t \text{ where } C_t = (r-\lambda)rI_t - rS_t + \lambda k E_{tt}$$

$$S_t = N'_t N_t.$$

For BIBD having parameters $v = \frac{k(k+1)}{2}$, $b = \frac{(k+1)(k+2)}{2}$, $r = k+2, k$, $\lambda = 2$ by application of (1·3) and (1·4) one can easily verify that between any two blocks there can be either 1 or 2 treatments common. Thus, the non-diagonal terms of S_t can be either 1 or 2. For small values of t, there are thus a manageably small number of S_t's and if for all such, $\det C_t \neq 0$, the design is impossible. Essentially this was the method employed by Connor to disprove the existence of (21, 28, 8, 6, 2) and (36, 45, 10, 8, 2)

Sometimes from two known BIBD's the existence or non-existence of a third BIBD can be decided. Thus, if an affine resolvable BIBD: $v = nk$, $b = nr$, r, k and λ and a symmetrical BIBD: $b' = v' = r$, $r' = k' = \lambda$, $\lambda' = (\lambda-1)/n$ both exist, then the symmetrical BIBD: $b'' = v'' = b+1$, $r'' = k'' = r$ and $\lambda'' = \lambda$ also exists. Hence if an affine resolvable BIBD (63, 93, 31, 21, 10)

and symmetrical BIBD (31, 31, 10, 10, 3) both existed, the symmetrical BIBD (94, 94, 31, 31, 10) would be possible. But the last design is known to be impossible and (31, 31, 10, 10, 3) is known to exist. Hence the affine resolvable BIBD (63, 93, 31, 21, 10) is impossible.

Shrikhande [5] has taken $t = b - v$ in (1·9) and has also utilised the Hasse–Minkowski invariant to establish the non-existence of a large number of affine resolvabe BIBD.

3. *Construction of BIBD*: The simplest BIBD for construction is perhpas the one with parameters v, $\binom{v}{k}$, $\binom{v-1}{k-1}$, k and $\binom{v}{k-2}$ obtained by taking all combinations of v varieties taken k at a time. From a given BIBD with incidence matrix N, we can obtain the complementary design with incidence matrix

$$E_{vb} - N$$

For this design $b' = b$, $v' = v$, $r' = b - r$, $k' = v - k$ and $\lambda' = b - 2r + \lambda$

From a given symmetrical BIBD, two other BIBD can be constructed by

(*i*) *Block Section* - Deletion of a block and all treatments contained in this block from other blocks. For the sake of definiteness, let the first block containing treatments 1, 2,....., k be deleted. The incidence matrix of the new design can be taken to be N_1 obtained by deletion of the 1st column and first k rows of N. The parameters of N_1 are then $v' = v - k$, $b' = b - 1$, $r' = r$, $k' = k - \lambda$ and $\lambda' = \lambda$.

(ii) *Block Intersection*— Deletion of a block and retention in other blocks only treatments contained in the deleted block. For the sake of definiteness, let the first block containing treatments 1, 2, ... , k be deleted. The incidence matrix of the new design can be taken to be N_2 obtained by deleting the 1st column and last $v - k$ rows. The parameters of the new design are $v' = k'$ $b' = b - 1$, $r' = r - 1$, $k' = \lambda$ and $\lambda' = \lambda - 1$.

Thus from the BIBD (16, 16, 6, 6, 2) we get BIBD (16, 16, 10. 10, 6), (10, 15. 6, 4, 2) and (6, 15. 5, 2, 1).

Let M be obtained from the incidence matrix N of a equi-replicate binary design by changing the null elements into -1. Then $M = 2N - E_{vb}$ and

$$MM' = 4NN' + (b - 2r)E_{vv} \qquad (1 \cdot 10)$$

From a Hadamard matrix of order $4t$ in the standard form, if we delete the first row and first column and call the resulting matrix M, then

$MM' = 4t\ I_{4t-1} - E_{4t-1,\ 4t-1}$. Hence $NN' = t\ I_{4t-1} + (t-1)\ E_{4t-1,\ 4t-1}$ from $(1 \cdot 10)$. Thus from a Hadamard matrix of order $4t$, we can construct the symmetrical BIBD : $b = v = 4t - 1$, $r = k = 2t - 1$, $\lambda = t - 1$. Hadamard matrices of order 2^n always exists. Hence, the existence of the symmetrical BIBD : $b = v = 2^n - 1$, $r = k = 2^{n-1} - 1$, $\lambda = 2^{n-2} - 1$.

If N be the incidence matrix of a BIBD (v, b, r, k, λ), $MM' = 4(r - \lambda)I_v + (b - 4r + 4\lambda)E_{vv} = 4(r - \lambda)I_v$ if $b = 4(r - \lambda)$ *i. e.* $2k = v \pm \sqrt{v}$. Let N_1 and N_2 be the incidence matrices of two BIBD $(v_1, b_1, r_1, k_1, \lambda_1)$, $(v_2, b_2, r_2, k_2, \lambda_2)$ such that $b_1 = 4(r_1 - \lambda_1)$, $b_2 = 4(r_2 - \lambda_2)$ and let M_1 and M_2 be the corresponding M-matrices. Then the design N obtained from the Kronecker product $M_1 \times M_2$ by changing -1 to 0, is a BIBD with parameters $b = b_1 b_2$, $v = v_1 v_2$, $r = r_1 r_2 + (b_1 - r_1)(b_2 - r_2)$, $k = k_1 k_2 + (v_1 - k_1)(v_2 - k_2)$ and $\lambda = 6r_1 r_2 - 8r_1 \lambda_2 - 8r_2 \lambda_1 + 12 \lambda_1 \lambda_2$. Note that $b = 4(r - \lambda)$ and hence it can also be used as a factor in forming the Kronecker product matrix representing yet another design. (4, 4, 3, 3, 2), (9, 12, 3, 4, 1), (16, 16, 6, 6, 2), (25, 40, 10, 16, 6), (36, 36, 15, 15, 6) are few designs of this type and many more designs can be constructed out of them. This method is due to Sillitto [6].

Sprott [7] has shown that it is possible to construct BIBD when block size is k and v is the integral power of an odd prime for the following values of λ. The design can be constructed by adding to the elements of GF (v) to the set of initial blocks B : $\left\{ x^{\beta + \gamma + \delta} \right\}$ where x is a primitive element of GF (v)

λ	q	γ	δ	β
$k(k-1)$	—	$0, 1, \ldots k-1$	0	$0, 1, 2, \ldots v-2$
$k(k-1)/q$	g. c. m. $(v-1, k)$	$0, \frac{v-1}{q}, \ldots, \frac{(q-1)(v-1)}{q}$	$0, 1, \ldots, \frac{k}{q}-1$	$0, 1, \ldots \frac{v-1}{q} - 1$

$\frac{k(k-1)}{2q}$	$g.c.m.(v-1, k)$	Do	Do	$0,1,\ldots, \frac{v-1}{2q} - 1$
	$2/(k-1), 2/(v-1)$			
$\frac{k(k-1)}{q}$	$g.c.m.(v-1, k-1)$	Do	$0,1,\ldots, \frac{k-1}{q} - 1$	$0,1,\ldots, \frac{v-1}{q} - 1$
$\frac{k(k-1)}{2q}$	$g.c.m.(v-1, k-1)$	Do	Do	$0,1,\ldots, \frac{v-1}{2q} - 1$
	$2/(v-1), 2/k$			

Many balanced incomplete block designs can be constructed from geometrical configurations and the two "module theorems" of Bose [8]. They are not specifically enumerated here as the results have found their places in existing text books.

If N be the incidence matrix of a BIBD with parameters v, b, r, k and λ, then the Kronecker product $E_{1t} \times N$ is the incidence matrix of a BIBD with parameters $(v, bt, rt, k, \lambda t)$. Thus, if a BIBD can be constructed in k-size blocks with v treatments and $\lambda = 1$, then a BIBD can be constructed in k-size blocks with v treatments and $\lambda = t$.

The methods employed in proving the falsity of Euler's conjecture have enabled us to have better insight into the structure of balanced incomplete block designs. Thus, if there be two BIBD exist with v_1 and v_2 treatments, the same block size k and $\lambda = 1$, then we can construct a BIBD in k-plot blocks with $\lambda = 1$, provided we can construct at least $k - 2$ mutually orthogonal latin squares of side v_2. In particular when k is a power of a prime, $B(v_1 v_2, k)$ is always possible. A number of such interesting results are given in [9].

Perhaps the most outstanding paper of recent years on the subject is the paper of Haim Hanani of the Department of Mathematics, Israel Institute of Technology, Haifa [10]. Prof. Hanani has shown that the necessary conditions for the existence of BIBD are also sufficient for $k = 3$ and $k = 4$, and he has proved the existence of a large number of BIBD's for $k > 4$.

4. *Bounds for number of common treatments between blocks.* In the case of symmetrical BIBD, between any two blocks, there can be exactly λ treatments in common. What can we say about the number of treatments common between two blocks when the BIBD is a symmetrical ? By putting $t = 2$ in (1·9) and remembering that $\det N^* N^{*\prime} \geqslant 0$, and denoting by x the number of treatments common between blocks 1 and 2, we get easily

$$(r-\lambda)^2 (k-\lambda)^2 - (\lambda k - rx)^2 \geqslant 0$$

whence $$-(r-\lambda-k) \leqslant x \leqslant \frac{1}{r}\,[\,2k + r(r-\lambda-k)\,] \qquad (4\cdot1)$$

It will be found that when $r = k$ *i. e.* when the BIBD is symmetrical both the bounds coincide and become λ.

Several attempts have been made in recent years to improve the bounds in (4·1). Let the first block contain treatments $1, 2, \ldots, k$ and the common treatments between the first and second block be $1, 2, \ldots, x$. Let N_1 be the matrix obtained from N by retaining the first k rows. Then just as in the derivation of (1·3) and (1·4), we get

$$x + l_2 + \ldots + l_{b-1} = k(r-1)$$

and $$x^2 + l^2{}_2 + \ldots + l^2{}_{b-1} = (r-\lambda)\,k + (\lambda-1)\,k^2$$

Let $\bar{l} = (l_2 + \ldots + l_{b-1})/(b-2)$

$\because \sum_{i=2}^{b-1} (l_i - \bar{l})^2 \geqslant 0$, we have

$$(r-\lambda)k + (\lambda-1)k^2 - x^2 - \frac{[\,k(r-1)-x\,]^2}{b-2} \geqslant 0$$

whence we obtain

$$\frac{k(r-1)}{b-1} - \sqrt{b-2}\;\mathrm{A} \leqslant x \leqslant \frac{k(r-1)}{b-1} + \sqrt{b-2}\;\mathrm{A} \qquad (4\cdot2)$$

where $$\mathrm{A}^2 = \left[k(r-\lambda) + (\lambda-1)k^2 - \frac{k^2(r-1)^2}{b-1}\right]/(b-1)$$

It will be noted that $A = 0$ when $r = k$ *i.e.* when the BIBD is symmetrical. This result is due to Trehan, A. M. [11]

5. *Conclusion.* In the 1938 edition of Fisher and Yates Statistical Tables for Biological, Agricultural and Medical Research (Oliver & Boy Ltd.) is listed a number of balanced incomplete block designs in the range $r \leqslant 10$ about whose existence or non-existence nothing was known. Except the cases (46, 69, 9, 6, 1) and (51, 85, 10, 6, 1) all other cases have been solved. After Hainan's paper. the establishment of sufficient conditions for $k \geqslant 5$ remains to be tackled Combinatorial problems have a peculiar appeal to the Indian mind and more papers have been contributed by Indians on this subject than by workers in any other country. The problems still before us will stimulate fresh workers to take up the work from the stage left by their elders.

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II

ORTHOGONAL LATIN SQUARES

1. *Introduction.* A Latin Square of order v is an arrangement of v symbols, say $1, 2, \ldots, v$ in a $v \times v$ square such that each symbol occurs once in every row and every column. Two latin squares are said to be orthogonal, if on superposition, each symbol of the first square occurs once with each symbol of the second square. A set of mutually orthogonal latin squares (*m.o.l.s.*) is a set of latin squares any two of which are orthogonal.

Let

$$N(v) = \text{maximum number of } m.o.l.s. \text{ of order } v$$

$$n(v) = \text{Min}\,(p_1^{n_1}, p_2^{n_2}, \ldots, p_u^{n_u}) - 1$$

where $v = p_1^{n_1} p_2^{n_2} \ldots p_u^{n_u}$

is the canonical prime power decomposition of v. Then it is well known that

$$n(v) \leqslant N(v) \leqslant v - 1$$

It is said that in the Russian Court, Euler was asked to arrange 36 officers belonging to 6 different ranks and 6 different regiments in a square array of order 6 so that each rank and each position is exactly once in every row and every column. The problem is equivalent to the construction of two *m. o. l. s.* of side 6. Euler could not solve the problem and in 1782 just one year before his death was published [1] his famous conjecture that two *m.o.l.s.* of order v when $v \equiv 2 \mod 4$ does not exist. Readers of Euler's biography must be knowing that Euler became totally blind in 1767 and he conceived this result in the inner world of a blindman's imagination. For $v \equiv 2 \mod 4$, $n(v) = 1$ and on the strength of Euler's conjecture $N(v) = 1$. For $v = p^n$, a prime power $n(v) = N(v) = p^n - 1$. In 1922, Mac Neish [2] conjectured that for all v, $N(v) = n(v)$. In 1958, E. T. Parker [3] proved that if a BIBD with parameters v, b, r, k and $\lambda = 1$ exist where k is a prime power, then $N(v) \geqslant k-2$. We know that the BIBD: $v = b = 21$, $r = k = 5$, $\lambda = 1$ exists. Hence $N(21) \geqslant 3$ but $n(21) = 2$. Hence Mac Neish's conjecture is disproved. This cast a doubt on Euler's conjecture itself. In a series of papers published in 1958, 1959 and 1960 R. C. Bose, S. S. Shrikhande and E. T. Parker ([4], [5]) proved that $N(v) \geqslant 2$ for $v > 6$. Hence Euler's conjecture is false for $v > 6$. For $v = 6$, Tarry [6] and later Fisher [7] verified by complete enumeration that $N(6) = 1$. Hence, if a positive integer $v > 2$ is called Eulerian when two

orthogonal latin squares of side v exists, then 6 is the only Eulerian number. This sensational demonstration of the falsity of Euler's nearly 200 years old conjecture made front page news in American newspapers. This topic has been chosen for the present discussion because the results are very recent and also because two Indians have played leading roles in removing the veil of mystery surrounding problem once for all.

2. *Preliminary Requisites.* $A(v^2, k)$ is an arrangement of v distinct objects in a $k \times v^2$ matrix such that in any two rows of the matrix all possible ordered pairs (i, j) of the v symbols occur exactly once.

Theorem 1. $N(v) \geqslant (k-2) \rightarrow A(v^2, k)$ and conversely.

Proof: (i) $N(v) \geqslant (k-2)$. In this case $(k-2)$ *m. o. l. s.* of side v exist. Let the first row of each square be in the standard form 1 2 ... v and R_{ij} denote the jth row of the ith square ($i = 1, 2, \ldots, k-2$; $j = 1, 2, \ldots, v$). Then the following $k \times v^2$ matrix is A (v^2, k)

$$
\begin{array}{cccccccccccccc}
 & 1 & 2 & \ldots & v & 1 & 2 & \ldots & v & 1 & 2 & \ldots & v & \ldots & 1 & 2 & \ldots & v \\
 & 1 & 1 & \ldots & 1 & 2 & 2 & \ldots & 2 & 3 & 3 & \ldots & 3 & \ldots & v & v & \ldots & v \\
(*) & 1 & 2 & \ldots & v & \multicolumn{3}{c}{R_{12}} & & \multicolumn{3}{c}{R_{13}} & & \ldots & & \multicolumn{2}{c}{R_{1v}} & \\
 & 1 & 2 & \ldots & v & \multicolumn{3}{c}{R_{22}} & & \multicolumn{3}{c}{R_{23}} & & \ldots & & \multicolumn{2}{c}{R_{2v}} & \\
 & \ldots & \ldots & \ldots & \ldots & \multicolumn{3}{c}{\ldots} & & \multicolumn{3}{c}{\ldots} & & \ldots & & \multicolumn{2}{c}{\ldots} & \\
 & 1 & 2 & \ldots & v & \multicolumn{3}{c}{R_{k-2,\,2}} & & \multicolumn{3}{c}{R_{k-2,\,3}} & & \ldots & & \multicolumn{2}{c}{R_{k-2,\,v}} &
\end{array}
$$

(ii) $A(v^2, k) \rightarrow N(v) \geqslant k - 2$

Take the first two rows of $A(v^2, k)$ to coordinatise the cells of a square array of order v. Corresponding to any one of the remaining $(k-2)$ rows, we form a square by putting in the cell (i, j) the symbol which occurs in that row in the corresponding position. The squares so formed are latin and any two of them are mutually orthogonal.

N. B. — By removing the second row and first v columns from (*) we get a $(k-1) \times v(v-1)$ matrix A* having v symbols such that in any two rows of the matrix every (i, j), $i \neq j$ occur exactly once.

Theorem 2. Let $v \varepsilon B\ (K, 1)$ where $K = \{k_1, k_2, \ldots, k_l;\ k_{l+1}, \ldots, k_m\}$ Let there be b_i blocks of size k_i and let the blocks having sizes $k_1, k_2, \ldots, k_l$ be disjoint. Let $q = \text{Min}\ \{1 + N(k_1), \ldots, 1 + (N(k_l), N(k_{l+1}), \ldots, N(k_m)\}$ Then $A(v^2, q+1)$ exists and hence $N(v) \geqslant q - 1$.

Proof: $N(k_i)$ *m. o, l. s.* of side k_i exist and this leads to $A(k_i^2, N(k_i) + 2)$. Write this array with the symbols of each block containing k_i treatments for $i = 1, 2, \ldots, l$, and retain only the first $q + 1$ rows. In this way we get a $(q + 1) \times \sum_{i=1}^{l} k_i^2 b_i$ matrix. Corresponding to each block size k_i, $i = l + 1, \ldots, m$ we can get a $[N(k_i) + 1] \times k_i(k_i - 1)$ matrix A*. Retain only the first $(q+1)$ rows. Suffix a $(q+1) \times v_2$ matrix $\underset{(q+1),\ 1}{E} \times [t_1, t_2, \ldots, t_{v_2}]$ where $v_2 = v - \sum_{i=1}^{l} k_i b_i$ and $t_1, t_2, \ldots, t_{v_2}$ are the symbols not contained in the disjoint blocks of sizes $k_1, k_2, \ldots, k_l$.

Note that $v^2 = \sum_{i=1}^{l} k_i^2 b_i + \sum_{i=l+1}^{m} k_i(k_i-1)b_i + v - \sum_{i=1}^{l} k_i b_i$ and the $(q + 1) \times v^2$ matrix so formed is $A(v^2, q + 1)$.

Corollary 1. If $v \varepsilon B(k, 1)$, then $N(v) \geqslant N(k) - 1$. If further k is a prime power $N(k) = k - 1$, and $N(v) \geqslant k - 2$. It is a direct consequence of Theorem 2. This result enabled Parker to disprove Mac Neish's conjecture as has been pointed out in the introduction.

Corollary 2. If $v \varepsilon B(k, 1)$ then $v - 3 \varepsilon B(K, 1)$ where

$K = \{k, k-1, k-2\}$ and by theorem 2

$N(v - 3) \geqslant \text{Min}\ \{1 + N(k - 2), N(k), N(k - 1)\} - 1.$

Proof: From the BIBD $(v, k, 1)$ we remove three treatments t_1, t_2, t_3 not belonging to the same block. Since in the original design a pair of treatments occurs only in one block, the three blocks containing (t_1, t_2), (t_2, t_3) and (t_1, t_3) have no treatment in common and are thus disjoint. The other block sizes are k and $k-1$. Application of Theorem 2 now establishes the corollary.

Example 1. Since BIBD $(v, 5, 1)$ exist for $v = 21, 41, 45$ and 65 there exists at least two *m. o. l s.* of side 18, 38, 42 and 62.

Corollary 3. If a resolvable BIBD $(v, k, 1)$ exists, then

$$N(v+r-1) \geq \text{Min } \{1+N(k),\ 1+N(r-1),\ N(k+1)\} - 1$$

Proof : $r-1$ treatments $\theta_1, \theta_2, \ldots, \theta_{r-1}$. To each block of the ith replication, add the new treatment θ_i, $i=1, 2, \ldots, r-1$ and add a new block $\theta_1, \theta_2, \ldots, \theta_{r-1}$. The blocks of the last replication and this new block are disjoint. Application to Theorem 2 now establishes the corollary.

Example 2. The resolvable BIBD : $v=21$, $b=70$, $r=10$, $k=3$, $\lambda=1$ exists. Hence $N(30) \geq 2$.

Let R be the ring of residue classes mod $(2m+1)$. Let A_0 be a 4-rowed matrix consisting of the elements θ of R and $x_1, x_2, \ldots, x_t$ where $N(t) \geq 2$. Define $x_j + \theta = x_j$, $j = 1, 2, \ldots, t$ and $\theta \in R$. Let A_θ be obtained from A_0 by adding θ to all its elements. Let $A^{**} = [A_0, A_1 \ldots, A_{2m}]$, $A^{***} = A(t^2, 4)$ with $x_1, x_2 \ldots, x_t$ and E be the Kronecker product $E_{41} \times [0\ 1\ 2\ \ldots\ 2m]$.

$$\triangle = [A^{**}, A^{***}, E] \ldots\ldots\ldots (**)$$

Theorem 3A. If $N(m) \geq 2$, then $N(3m+1) \geq 2$.

Proof : Let

$$A_0 = \begin{bmatrix} 0 & 0 & \ldots 0 & 1 & 2 & \ldots m & 2m & 2m-1 & \ldots m+1 & x_1 & x_2 \ldots x_m \\ 1 & 2 & \ldots m & 0 & 0 & \ldots 0 & x_1 & x_2 & \ldots x_m & 2m & 2m-1 \ldots m+1 \\ 2m & 2m-1 & \ldots m+1 & x_1 & x_2 & \ldots x_m & 0 & 0 & \ldots 0 & 1 & 2 \ldots m \\ x_1 & x_2 & \ldots x_m & 2m & 2m-1 & \ldots m+1 & 1 & 2 & \ldots m & 0 & 0 \ldots 0 \end{bmatrix}$$

Then $\triangle$ as in (**) is $A\left(\overline{3m+1}^{2}, 4\right) \to N(3m+1) \geq 2$.

Example 3. Taking $m = 3.\ 7,\ 11,\ 15,\ 19$ we get $N(v) \geq 2$ for $v = 10,\ 22,$ 34, 46 and 58

Theorem 3B $N(14) \geq 2$

Let

$$P_0 = \begin{bmatrix} 0 & x_1 & x_2 & x_3 \\ 1 & 0 & 0 & 0 \\ 4 & 4 & 6 & 9 \\ 6 & 1 & 2 & 8 \end{bmatrix}$$

$$A_0 = [P_0,\ P_1,\ P_2,\ P_3]$$

where P_1, P_2 and P_3 are obtained from P_0 by cyclic permutation of the rows. Then $\triangle$ as defined in (**) is $A(14^2, 4) \to N(14) \geq 2$

Theorem 3C, $N(26) \geq 2$

Let

$$P_0 = \begin{bmatrix} 0 & 0 & 0 & 0 & x_1 & x_2 & x_3 \\ 3 & 6 & 2 & 1 & 0 & 0 & 0 \\ 8 & 20 & 12 & 16 & 20 & 17 & 8 \\ 12 & 16 & 7 & 2 & 19 & 6 & 21 \end{bmatrix}$$

$$A_0 = [P_0,\ P_1,\ P_2,\ P_3]$$

where P_1, P_2 and P_3 are obtained from P_0 by a cyclic permutation of the rows. Then Δ as defined in (**) is $A(26^2, 4) \to N(26) \geq 2$.

Theorem 4. If $k \leq N(m) + 1$, then

(i) $N(km+1) \geq \text{Min}\ \{1+N(m+1), N(k), N(k+1)\} - 1$

(ii) $N(km+x) \geq \text{Min}\ \{1+N(m), 1+N(x), N(k), N(k+1)\} - 1$ when $1 < x < m$.

Proof: Let A_k^* be the first k rows of $[N(m) + 1] \times m(m-1)$ matrix A^* in the note of Theorem 1. Let $\Delta_k = [A_k^*, P_k]$ where P_k = the Kronecker product $E_{k1} \times [1\ 2\ \ldots\ m]$. Let the symbols in 1, 2, ..., m in the jth row of Δ_k be replaced by $t_{(j-1)m+1}, t_{(j-1)m+2} \ldots t_{jm}$, $j = 1, 2, \ldots, k$. To the $(i-1)m + j$th column n introduce θ_i, $1 \leqslant j \leqslant m$, $i = 1, 2, \ldots, x$. Introduce k new columns $t_1, t_2, \ldots, t_m$; $t_{m+1}, t_{m+2}, \ldots, t_{2m}$; $t_{(k-1)m+1}, t_{(k-1)m+2}, \ldots, t_{km}$. For $x = 1$, we get 4 (i) from Theorem 2. For $1 < x < m$. introduce a new column $\theta_1, \theta_2, \ldots, \theta_x$. Applying Theorem 2 we get 4 (ii).

Example 4. In Theorem 4 (i) taking $k = 7$, $m = 7$, we get $N(50) \geqslant 5$

In Theorem 4 (ii) taking

$k = 7$, $m = 7$, $x = 5$ we get $N(54) \geqslant 4$

$k = 7$, $m = 9$, $x = 3$ we get $N(66) \geqslant 2$

$k = 4$, $m = 16$, $x = 10$ we get $N(74) \geqslant 2$

$k = 4$, $m = 16$, $x = 14$ we get $N(78) \geqslant 2$

$k = 4$, $m = 19$, $x = 10$ we get $N(18) \geqslant 2$

3. *Proof of falsity of Euler's conjecture*: Let v be of the form $4t + 2$ where $t > 1$. From examples 1, 2, 3, 4, Theorem 3B and Theorem 3C we see that $N(v) = N(4t + 2) \geqslant 2$ for $t = 2, 3, \ldots 21$. Any v of the form $4t + 2$ in the closed interval (a_i, b_i) below can be expressed as $4m_i + x_i$, $10 \leqslant x_i \leqslant c_i < m_i$

i	1	2	3	4	5	6	7	8	9	10	11	12	13
a_i	90	102	118	134	158	186	222	266	314	378	458	554	666
b_i	98	114	130	154	182	218	262	310	374	454	550	662	726
m_i	20	23	27	31	37	44	53	64	76	92	112	136	164
c_i	18	22	22	30	34	42	50	54	70	86	102	118	70

Hence for every v of the form $4t + 2$, $10 \leqslant v \leqslant 726$, $N(v) \geqslant 2$ by Theorem 4(*ii*) Thus it is sufficient to prove the theorem for numbers $v \equiv 2 \bmod 4$ and $v \geqslant 730$

$$v - 10 = 144g + 4u,\ g \geqslant 5,\ 0 \leqslant u \leqslant 35$$

$$\therefore\ v = 4(36g) + 4u + 10$$

$N(36g) \geqslant n(36g) \geqslant 3$. Hence if in Theorem 4(*ii*) we take $k = 4$, $m = 36g$, $x = 4u + 10$, $10 \leqslant x \leqslant 150 < 180 \leqslant m$. Hence $1 < x < m$ and $N(x) \geqslant 2$. Therefore, $N(v) \geqslant 2$. This completes the proof of the falsity of Euler's conjecture for $v > 6$.

4. *Conclusion.* Chowla, Erdos and Straus [8] have proved that $N(v) \to \infty$ as $v \to \infty$. The evaluation of $N(v)$ when v is not a prime power, still remains to be tackled. Improving of lower bounds for $N(v)$ presents problems of research to new workers. Finney [9] has aptly remarked that this solution to a problem nearly 200 years old is a remarkable achievement and the sharp technique employed will open the door for new research in this fascinating subject.

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BINARY ERROR CORRECTING CODES

1. Introduction. A binary channel can transmit one of two symbols 0 and 1. Due to the presence of disturbance or 'noise' a transmitted 1 may be received as 0 or a transmitted 0 may be received as 1. A v-letter n-place binary signalling alphabet A_n may be defined as v distinct n-place sequences α_0, α_1,.....α_{v-1} such that each place is occupied by 0 or 1. Given a set of v distinct messages, we get an encoder $E_{n,v}$ by setting up a (1, 1) correspondence between the messages and the sequence of the alphabet. To transmit a message over the channel the n individual symbols of the corresponding sequence are presented to the channel in succession. The output is then an n-place binary sequence belonging to the set B_n of all possible 2^n binary sequences. A decoder $D_{n,v}$ is obtained by partitioning B_n into v disjoint sets S_0, S_1,.....S_{v-1} and setting up a correspondence between these subsets and the sequence of the alphabet so that if a sequence β_i belonging to S_i is received as an output, it is read as the sequence α_i as the corresponding message. The encoder $E_{n,v}$ and the decoder $D_{n,v}$ taken together constitute an n-place binary code. If all β_i which does not differ from α_i in more than t places belong to S_i ($i=0, 12,\ldots\ldots v-1$), then if there are t or lesser number of errors in transmission, the received message will be correctly interpreted. Such a code will be called a *t-error correcting n-place binary code.* Perhaps the following example of an 1-error correcting 5-place binary code will make the ideas clearer

Messages	Alphabet A_5	B_5			
		S_0	S_2	S_2	S_3
Halt	00000...α_0	00000	01110	11001	10111
Attack	01110...α_1	10000	11110	01001	10111
Retreat	11001...α_2	01000	00110	10001	11111
Advance	11011...α_3	00100	01010	11101	10011
		00010	01100	11011	10101
		00001	01111	11000	10110
		00011	01101	11010	10100
		10010	11100	01011	00101
Decoded Message		Halt	Attack	Retreat	Advance

2. *Definitions and Preliminary Results.* Let γ be an n–place vector whose coordinates are elements of GF(2). By the weight of γ we shall understand the number of non-zero coordinates in γ. We shall denote it by $w(\gamma)$. The Hamming distance $\delta(\gamma_1, \gamma_2)$ between two n–vectors γ_1, γ_2 with coordinates in GF(2) may be defined as the number of places in which the two vectors differ. Hence

$$\delta(\gamma_1, \gamma_2) = w(\gamma_1 + \gamma_2)$$

Slepian [1] discusses a particular class of codes for which $v = 2^k$ and the letters of the alphabet A_n form a *subgroup* of B_n. The null sequence (0 0 ... 0) is the unit element of B_n and belongs to A_n.

Let $u = 2^{n-k}$. Consider

$$\begin{array}{llll} \alpha_0 + \gamma_0 & \alpha_1 + \gamma_0 & \ldots\ldots & \alpha_{v-1} + \gamma_0 \\ \alpha_0 + \gamma_1 & \alpha_1 + \gamma_1 & \ldots\ldots & \alpha_{v-1} + \gamma_1 \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ \alpha_0 + \gamma_{u-1} & \alpha_1 + \gamma_{u-1} & \ldots\ldots & \alpha_{v-1} + \gamma_{u-1} \end{array}$$

where $\gamma_0 = (0, 0, \ldots, 0)$ and γ_j $(j = 1, 2, \ldots, u-1)$ does not occur in

$$\begin{array}{llll} \alpha_0 + \gamma_0 & \alpha_1 + \gamma_0 & \ldots\ldots & \alpha_{v-1} + \gamma_0 \\ \alpha_0 + \gamma_1 & \alpha_1 + \gamma_1 & \ldots\ldots & \alpha_{v-1} + \gamma_1 \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ \alpha_0 + \gamma_{j-1} & \alpha_1 + \gamma_{j-1} & \ldots\ldots & \alpha_{v-1} + \gamma_{j-1} \end{array}$$

Let β_j $(j = 0, 1, 2, \ldots\ldots u-1)$ be the leader * of the coset $(\alpha_i + \gamma_j)$, $i = 0, 1, 2, \ldots a-1$. Take S_i to be the set $(\alpha_i + \beta_j)$, $j = 0, 1, 2, \ldots, u-1$. Then the system will be called a (n, k) binary group code. We can establish the following sets of necessary and sufficient conditions for a (n, k) binary group code to be t–error correcting.

I If $\beta \in B_n$, $w(\beta) \leqslant t$, then β is a coset leader

II $w(\beta_i) \geqslant 2t + 1$, $i = 1, 2, \ldots, v-1$

III A n x (n-k) matrix of rank (n-k) with elements from GF(2) exists such that any 2t rows are independent.

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* Let $\beta \in B_n$. By the leader of the coset $(\alpha_i + \beta)$, $i = 0, 1, 2, \ldots, u-1$ we shall understand a member whose weight does not exceed the weight of any other member of the coset.

TEXTURAL CHARACTERISTICS AND DEPOSITIONAL ENVIRONMENT OF THE NEYVELI AQUIFER SANDS

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ABSTRACT

Fifty eight borehole samples from the Neyveli aquifer sands were mechanically analysed and their texture determined. The statistical distribution of the grain size parameters were studied in detail. Scatter diagrams of grain size parameters are used to discuss the depositional environment. It is concluded that the aquifer – I sands are derived from two different sources, which were transported by two different streams and deposited together in the Neyveli basin.

INTRODUCTION

In a number of places, along the Coromandal coast of India, the Cuddalore sandstones, sediments of Miocene age, are exposed. In the neighbourhood of Neyveli, the Cuddalore series show the following lithologic succession.

Recent and sub-recent red soils

Soft, mottled sandstones and clay lenses

Average thickness – 180'

White clays, *0 to 20' thick*

Lignite, *Average thickness – 50'*

White under clays, *0 to 20' thick*

Aquifer I – waterlogged sands

Average thickness – 50'

Lenses and blankets of clay

0 to 20′ thick

Aquifer II – waterlogged sands

Average thickness – 50′

Lenses and blankets of clay

0 to 50′ thick

Aquifer III – waterlogged gravel,

sands and sandstones

thickness – > 1000′?

Eocene and Cretaceous sediments

Precambrian crystallines

The true nature of these Tertia y sediments and their sedimentological charaters are not fully known. Vredenburrg, E. W. (1908) and Pilgrim, G. E. (1910) are the pioneers to work on these sediments. Then, for nearly a quarter of a century, the Cuddalore sandstones did not attract any attention. Around 1930, Lignite was first noted; since then a few publications on lignite, stratigraphy and structure of this basin have come out, but none of them have much bearing on the sedimentology. (Krishnan, M. S., 1956; Jones, P. H., and Subramaniam, V., 1961).

In this department sedimentological studies of some Tertiary formatoins of the eastern coast of India are under progress. This paper deals with the textural characteristics of the waterlogged sands styled as Aquifer I. Certain physical characteristics of the depositional environment, as revealed by the study of grain size distribution, are discussed.

METHODS

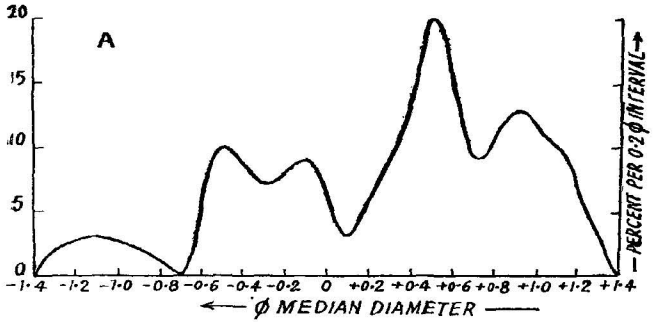
Sambles for study were collected while brilling pumpwells and liginite-exploratory boreholes. Since the samples were unconsolidated sands, no

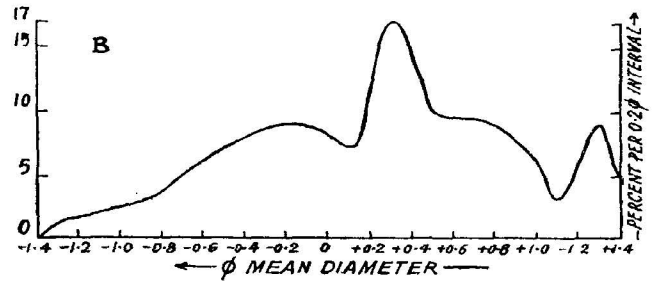
mechanical or chemical disaggregation was necessary. The samples were boiled in dilute hydrochloric acid to remove minor authigenic coatings and stains. About 500 grams of washed and dried sample was sieved through a set of DIN 1171 type sives on an automatic sieve-shaker. Fractions retained on every sieve were weighed correct to 0·01 of a gram.

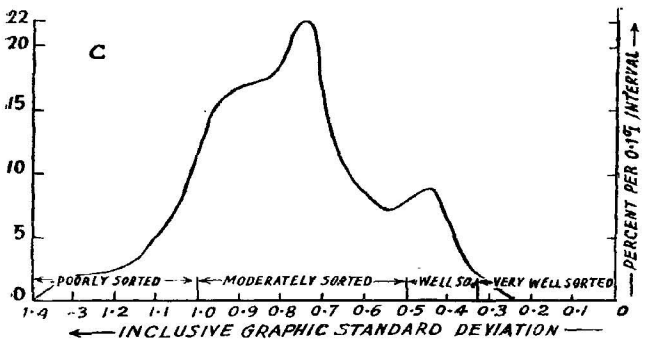
Frequency curves were drawn and the modal diameters were determined Cumulative curves were drawn and necessary percentiles read off the curves for computing the Statistical parameters. Four such parameters, namely, Mean-size, Standard deviation, Skewness and Kurtosis were calculated using Folk's (1955) inclusive formulae.

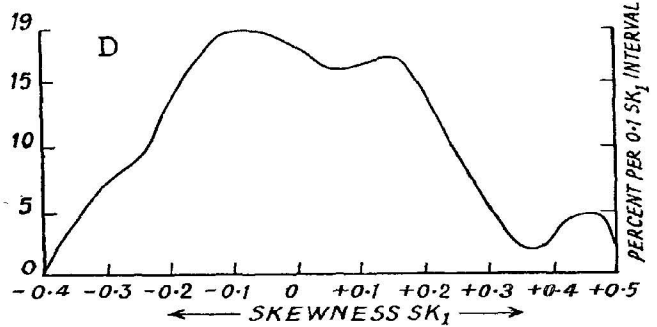
The distribution of the grain-size parameters for the 58 samples were studied statistically. The Median and the Mean-size distributions were studied by classifying them at 0.2 Ø interval, the Standard deviation at 0.1 Ø interval, the Skewness at 0.1 interval and Kurtosis at 0.02 (K'_g) interval. Figures 1 A to 1 E are frequency curves, and figure-2 gives cumulative curves illustrating the distribution of the grain-size parameters. Statistical distribution parameters of the grain-size parameters were calculated and are listed in table-2.

The interrelations between the grain-size parameters, which help in deciphering the environment of deposition, were studied by means of scatter diagrams shown in Figs. 3 & 4.









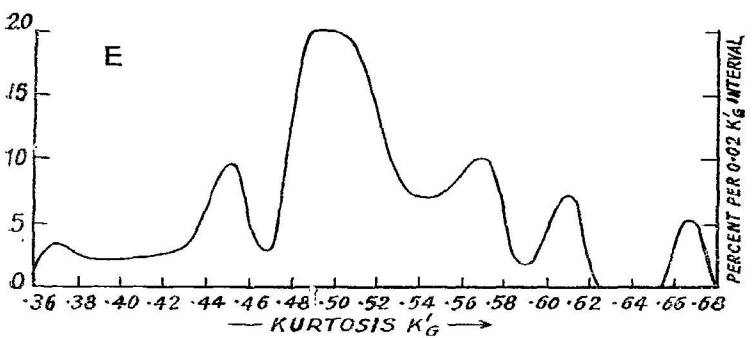


Fig. 1. A—Frequency curve of ϕ Md values
B—Frequency curve of ϕ Mz values
C—Frequency curve of σI values
D—Frequency curve of Sk_I values
E—Frequency curve of K'_G values

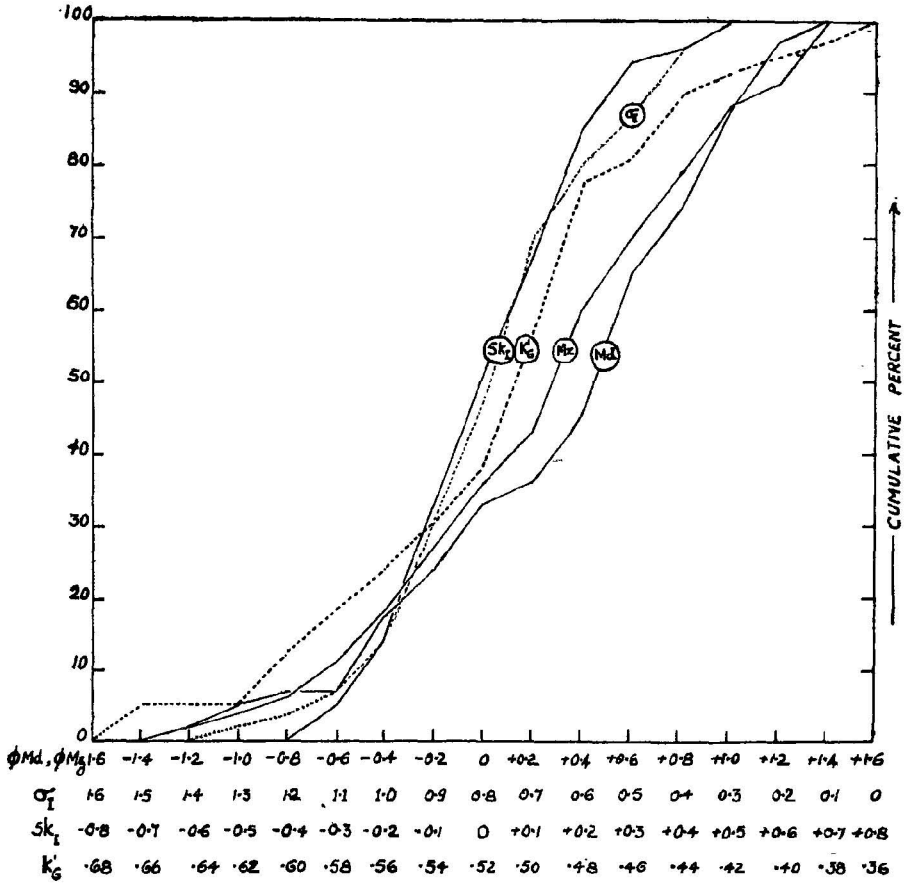


Fig. 2. Cumulative curves illustrating the distribution of grain-Size parameters in the 58 samples.

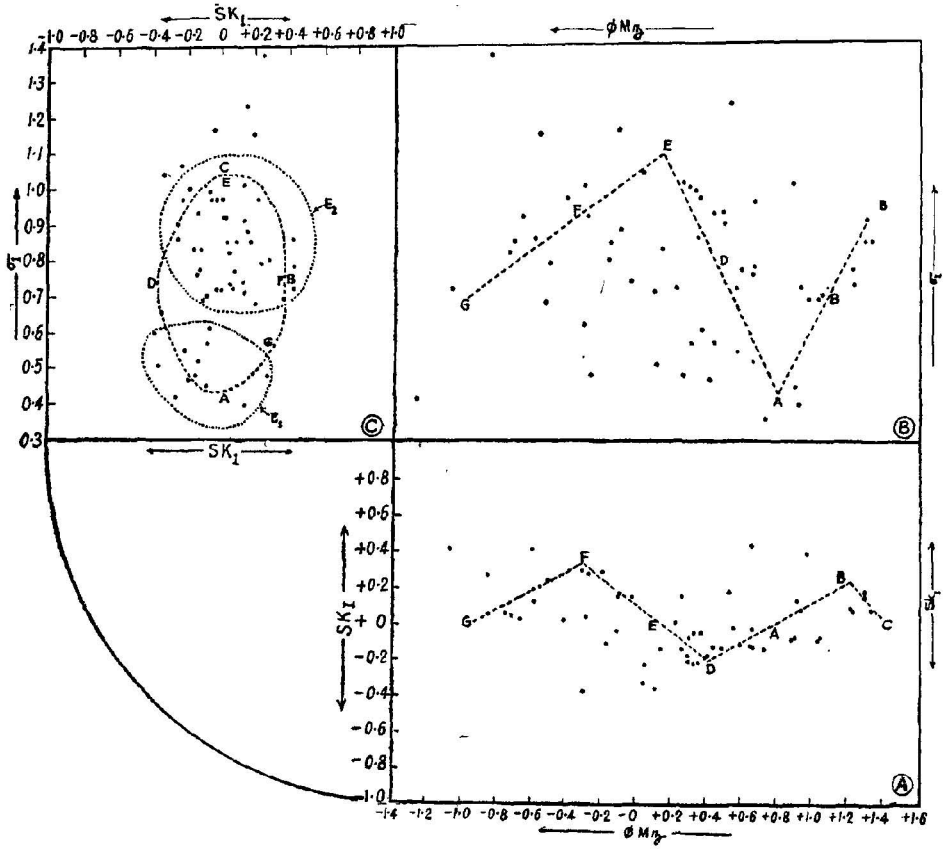


Fig. 3. Scatter diagram of (A) Mz vs. Sk_I (B) Mz vs. σI and (C) Sk_I vs. σI

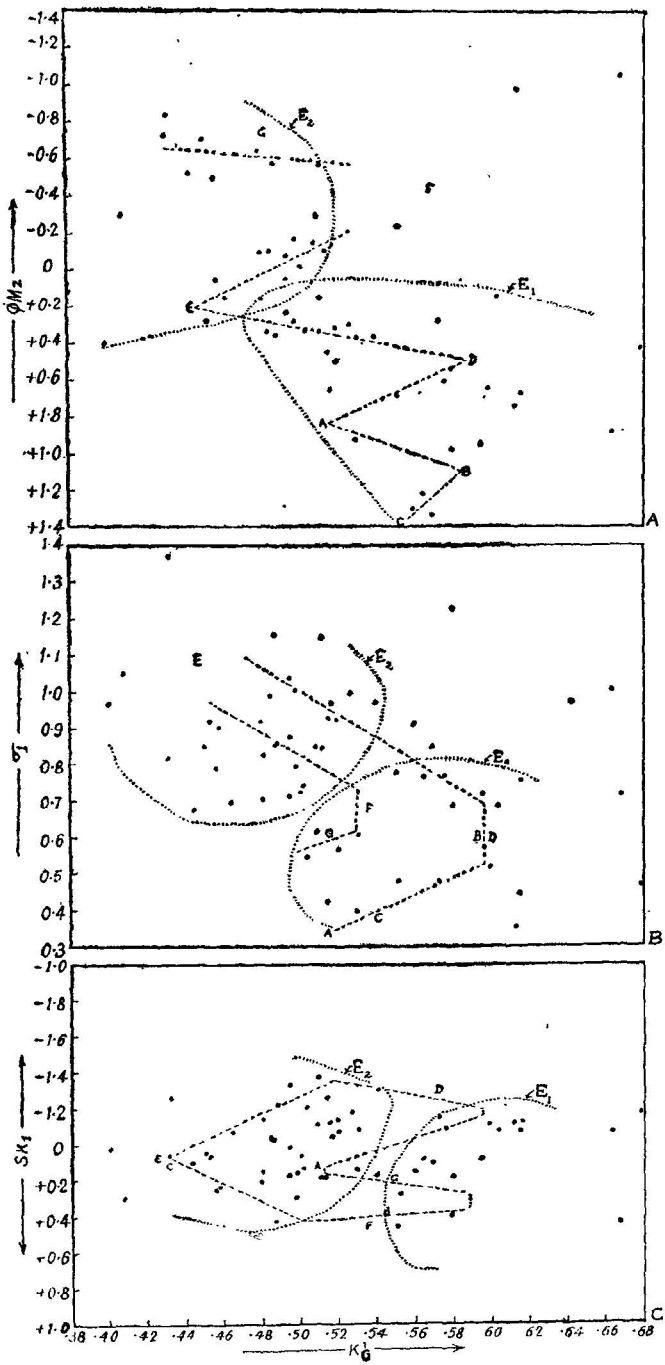


Fig. 4. Scatter diagram of (A) K'_G vs. Mz,
(B) K'_G vs (C) K'_G vs. Sk_I

Sample index	ϕ Mode			Average size		Standard Deviation σI	Skewness Sk_I	Kurtosis K'_G
	Primary	Secondary	Weak	ϕ Md	ϕ Mz			
101	+0.6	−0.3	+1.2	+0.56	+0.44	0.93	−0.13	.5146
105	+0.6	−0.3	+1.2	+0.64	+0.56	0.72	−0.03	.2995
107	+0.6	−0.3	> −1.32	+0.27	+0.04	1.04	−0.33	.4935
109	+0.6	+1.2	−0.3	+0.60	+0.49	0.93	−0.15	.5190
114	+0.6	−0.3	+1.2	+0.50	+0.36	0.97	−0.22	.5317
123	+0.6	−0.3	+1.2	+0.46	+0.35	0.86	−0.23	.4876
132	+0.2	+0.9	−1.2	+0.29	+0.05	0.90	−0.23	.4581
16	+0.6	+1.2	−0.3	+0.67	+0.41	0.47	−0.18	.6775
3	+2.0	+0.6	+1.2	+1.09	+1.04	0.70	−0.08	.4618
7	+1.2	+0.6	+2.0	+1.03	+0.90	0.45	−0.08	.6139
103	+1.2	+0.6	+2.0	+0.89	+0.94	0.72	+0.07	.5943
104	+1.2	+2.0	+0.6	+1.15	+1.23	0.73	+0.06	.4995
106	+1.2	+2.0	+0.6	+1.22	+1.33	0.85	+0.09	.5679
108	+1.2	+2.0	+0.6	+1.15	+1.22	0.77	+0.08	.5639
112	+1.2	+2.0	> −1.32	+1.22	+1.30	0.91	+0.14	.5588
118	+1.2	+0.6	+0.3	+0.96	+0.88	1.01	−0.09	.6625
119	+1.2	+0.6	+2.0	+1.06	+1.03	0.69	−0.10	.6029
129	+1.2	+2.0	+0.6	+1.17	+1.29	0.85	+0.17	.5113
135	+0.6	+1.2	nil	+0.94	+0.92	0.40	+0.12	.5290
8	+1.2	+0.6	−0.3	+0.89	+0.65	0.52	−0.13	.5977
15	+1.2	+0.6	−0.3	+0.86	+0.73	0.36	−0.14	.6116
113	+0.6	+1.2	−0.3	+0.76	+0.66	0.76	−0.13	.6145
120	+0.6	+1.2	−0.3	+0.67	+0.60	0.77	−0.12	.5753
121	+0.6	−0.3	+1.2	+0.67	+0.67	0.78	−0.43	.5503
130	+1.2	+0.6	+2.0	+0.97	+0.97	0.69	+0.38	.5790
134	+0.6	+1.2	+2.0	+0.69	+0.67	0.97	−0.04	.5159

Table—1 (contd.) Statistical parameters of grain-size.

Sample index	ϕ Mode			Average Size		Standard Deviation σ I	Skewness Sk_I	Kurtosis K'_G
	Primary	Secondary	Weak	ϕMd	ϕMz			
1	−0.3	+0.6	+1.2	−0.27	−0.25	0.48	+0.27	.5513
2	−0.3	+0.6	+1.2	−1.27	−1.25	0.42	−0.26	.5136
5	−0.3	+0.6	+1.2	−0.43	−0.54	0.68	+0.20	.4433
6	−0.3	+0.6	+1.2	−0.38	−0.50	0.79	+0.24	.4562
12	−0.3	+0.6	+1.2	−0.27	−0.65	0.92	+0.02	.4789
13	−0.3	+0.6	+1.2	−0.44	−0.73	0.82	+0.05	.4307
14	−0.3	+0.6	+1.2	−0.44	−0.71	0.85	+0.04	.4503
102	−0.3	+1.2	+2.0	−0.14	−0.09	0.88	+1.60	.4939
115	>−1.32	−0.3	+0.6	−1.07	−0.84	1.37	+0.26	.4320
117	−0.3	+0.6	+2.32	−0.20	−0.10	0.71	+0.14	.4803
122	−0.3	+0.6	>−1.32	−0.07	−0.11	1.16	−0.04	.4859
124	>−1.32	−0.3	+0.6	−0.48	−0.30	1.05	+0.29	.4080
125	>−1.32	+0.6	+1.2	−1.16	−1.06	0.72	+0.41	.6682
127	−1.2	−0.3	+0.6	−0.83	−0.59	0.86	+0.41	.4866
128	−0.3	+0.6	+1.2	−0.32	−0.18	0.80	+0.28	.4978
131	−0.3	+0.6	+1.2	−0.13	−0.03	0.74	+0.14	.5008
133	−0.3	>−1.32	+0.6	−0.35	−0.40	0.97	+0.01	.3998
136	−0.3	+0.6	+1.2	−0.07	−0.58	1.15	+0.19	.5113
140	+0.2	>−1.32	+1.2	−0.26	−0.28	0.92	+0.03	.4530
11	−0.3	+0.6	+1.2	+0.32	−0.16	0.85	−0.11	.5075
139	−0.6	−0.3	+1.2	+0.56	−0.30	0.62	−0.39	.5086
4	−0.3	+0.6	+1.2	+0.27	+0.12	0.51	−0.36	.3671
110	−0.3	+0.6	+1.2	+0.44	+0.30	1.00	−0.18	.5264
111	−0.3	+0.6	+1.2	+0.18	+0.15	0.83	−0.15	.4804
116	−0.3	+0.6	+1.2	+0.41	+0.33	0.99	−0.05	.4843
126	−0.3	+0.6	+1.2	+0.15	+0.27	1.01	+0.14	.4973
137	−0.3	+0.6	+2.32	+0.43	+0.53	1.23	+0.17	.5789
138	−0.3	+0.6	+1.2	+0.25	+0.23	0.72	−0.003	.4941
9	+0.6	−0.3	+1.2	+0.58	+0.31	0.55	−0.21	.5031
10	+0.6	−0.3	+1.2	+0.60	+0.37	0.61	−0.06	.5297
17	+0.6	−0.3	+1.2	+0.51	+0.27	0.48	−0.15	.5719
18	+0.6	−0.3	+1.2	+0.51	+0.31	0.57	−0.08	.5192

Table—1. Statistical parameters of grain-size.

Measures of Distribution	Median ϕ Md	Mean-size ϕ Mz	Standard Deviation σI	Skewness Sk_I	Kurtosis K'_G
Mode, primary	+0.500	+0.300	0.750	−0.100	0.495
Mode, secondary	+0.900	+1.300	0.450	+0.150	0.570
Median	+0.440	+0.280	0.790	−0.010	0.508
Graphic Mean	+0.320	+0.243	0.776	−0.003	0.508
Standard Deviation	0.672	0.666	0.222	0.222	0.063
Skewness	−0.297	−0.098	−0.051	−0.057	+0.050
Kurtosis	0.894	0.922	1.064	1.187	1.311

Table—2. Statistical Parameters of Grain-size distribution parameters.

RESULTS AND DISCUSSION

Table-1 presents the the statistical parameters of grain-size distribution for the 58 samples. In table-2 the statistical parameters of Parameters ofgrain-size are given. These tables bring out the strong polymodal character of the aquifer sands. The distribution of Mean-size, Median-size, Sorting values, Skewness and Kurtosis are again non-normal and strongly polymodal. See also Figs· 1-A to 1-E and 2. Sediments of polygeneration origin usually have such characteristics. (Pettijohn, F. J., 1957; Folk, R. L., 1957).

The non-normal and polymodal distribution of the above five parameters could be rendered near-normal and fairly unimodal if the 58 samples are divided into three classes on the basis of modal and mean grain diameters. Such a division would group the first 19 samples under "Very coarse sands' class, the middle 19 under "Coarse sands" class and the last 20 under the "Medium sands" class, in table-1,

Texture of very coarse sands

Modal diameter:

$-0.3\ \phi$ is the most frequently occurring primary mode;

$-1.32\ \phi$ is the next dominent primary mode;

$-0.6\ \phi$ ls the most frequently occourring secondary mode;

$+1.2\ \phi$ in an insignificant, but very often occurring mode.

Median diameter:

modal Md: $-0.5\ \phi$, $-0.1\ \phi$ and $-1.1\ \phi$; generally moderately sorted, with a fine skewed distribution.

Mean diameter:·

modal Mz: $-0.1\ \phi$;

generally poorly sorted, with a fine skewed distribution.

Sorting:

modal σ I: $0.9\ \phi$, i.e., mostly poorly sorted;

poor sorting of σ I values.

Symmetry of distribution :

modal Sk_I : + 0.2, i.e., mostly fine skewed ; good sorting of Sk_I values.

Peakedness :

modal $K_G = 1.005$, i.e., mostly mesokurtic.

Show a good sorting of K_G values, with a skewness towards platykurtic nature.

Texture of Medium Sands :

Modal diameter :

+ 1.2 ø is the most frequently occurring primary mode,

+ 0.6 ø is the next dominant primary mode,

+ 1.2 ø is the most frequently occurring secondary mode wherever + 0.6 ø mode is the primary mode,

+ 0.6 ø is the next dominant secondary mode wherever + 1.2 ø mode is the primary mode.

+ 2.0 ø is also often a secondary mode.

− 0.3 ø and − 1.32 ø are also modes in a few samples but they are very insignificant modes.

Median diameter :

modal Md : + 0.9 ø ;

generally poorly sorted, with a coarse skewed distribution.

Mean diameter :

modal Mz : + 0.8 ø and + 1.3 ϕ ; very poorly sorted with coarse skewed distribution.

Sorting :

modal $\sigma I = 0.65\ \emptyset$, i.e., mostly moderate sorting, the σI are well sorted and unskewed.

Symmetry of distribution :

modal $Sk_I = 0.0\ \emptyset$ i.e. mostly symmetrical the Sk_I values are poorly sorted and show skewness towards coarse skewed distribution.

Peakedness :

modal $K_G = 1.55$, i.e., mostly leptokurtic the K_G values are moderately sorted and show symmetrical distribution.

The statistical parameters of the coarse sands grade into those of very coarse sands on one hand and into those of medium sands on the other. By a mixing of the bimodal medium sands with the nearly unimodal coarse sands, the non-normal polymodal distribution of the parameters of grain size could well be explained. It is therefore concluded that in the depositional basin, sediments of two different textures were mixed up.

When there is such a mixing of two different textural sand units, the 3-dimensional plot of σI, Mz and Sk_I gives a helical trend of plots for the samples with a rhythmic change in kurtosis. (Folk, R. L., 1957). Figure-3, a 2-dimensional projection of the 3-dimensional plot, brings out clearly the helical trend followed by the aquifer sands and figure-4 shows the rhythmic changes in kurtosis. The course of variation, in Figs.-3 & 4, is from C to G through B, A, D, E and F respectively. This single course of variation needs to be split into two different ones, namely A to G trend and A to C trend, for the following reasons. Plots around A are the most frequently occurring modal diameters in the medium sands and plots around G are the most frequently occurring modal diameters in the very coarse sands, so that by a mixing of these two the $A \rightarrow D \rightarrow E \rightarrow F \rightarrow G$ trend results. The $A \rightarrow B \rightarrow C$ is a subsidiary trend, resulting by mixing of fine sands to the medium sands by waning currents of a stream.

Evidences of mixing being certain, the question now arises as to what was the mechanism of such a mixing of the two textural units. For continental deposits of river origin anyone of the following three mechanisms could cause such a mixing.

1. Deposition by a youthful stream that normally brings say, medium sands, which however goes on floods often and brings in very coarse sands mixed up with medium and fine sands.

2. The provenance might have been a complex one which on weathering differentially would give rise to different textural groups of detritals. These could have been washed together into a depositional basin.

3. Two geographically different provenances might have supplied material by means of two different transportational channels which deposited material into the same basin.

The first mechanism is not the cause of mixing observed in the aquifer sands, for, deposits of a youthful river that often goes on spate are uniformly poorly sorted and show widely varying modes. In the aquifer sands there is a marked monotony of modal diameters; the very coarse as well as the medium sands have by themselves attained moderate to good sorting. This, together with extreme high and low values of kurtosis indicate the aquifer sands attained their sorting elsewhere in a high-energy environment and were transported without modification of their texture into a depositional basin where they were mixed with another type of material and were deposited.

That the second postulated mechanism is not also the cause of mixing, but the third is the mechanism that caused this is seen from scatter diagrams, Figs. 3 and 4. The use of scatter plots and their sensitiveness in distinguishing depositional environs is well known. (Mason, C.C., and Folk, R.L., 1958; Freidman, G.M., 1961; Folk, R.L., 1962). In Fig. 3, in the scatter diagram of skewness versus standard deviation, the plots form two distinct configurations, environs E_1 and E_2. Environ E_1 shows moderate sorting and symmetrical distribution of grain size. Environ E_2 shows poorer sorting and slightly fine skewed distribution. In fig.-4, E_1 is discerned to be medium-fine sands and show leptokurtic distribution, E_2 the coarse and very coarse sands that show meso to platykurtic distribution. These indicate that the sediments were derived from two different geographic provenances, which were brought into the depositional basin by two different streams.

Studies on the sphericity, roundness and shape of grains, the heavy mineral assemblage and field studies have also pointed towards two provenances and two different transportational channels for these sands. (Louisnathan, S. J., 1962).

CONCLUSIONS

1. The aquifer–I sands are unconsolidated and porous. Their texture in mainly very coarse to medium sands, that are moderately sorted, mostly coarse skewed and mesokurtic.

2. The polymodal character of the distribution of the statistical *parameters of grain-size, and the helical trend of variation of the scatter* plot (Mz, σI and Sk_I) with rhythmic changes of kurtosis points towards a mixing of two textural units in the depositional basin.

3. Monotony of modal diameters, and extreme low and high values of kurtosis indicates that the sediments received their sorting elsewhere and were brought into the depositional basin where they were mixed up with another textural unit.

4. The two-fold configuration of plots in the scatter diagrams brings out clearly that two different streams differentially transported the materia into the depositional basin.

ACKNOWLEDGEMENTS

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OCCURRENCE OF NORITE-ANORTHOSITE MASSES NEAR ABOUT ODDANCHATRAM, MADURAI DISTRICT, MADRAS STATE

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ABSTRACT

The occurrence of anorthosite rocks near about Oddanchatram, Madurai district is reported. A brief description of the occurrence and petrology of the rocks is given pending detailed field and laboratory nvestigations. The rocks are considered to be of Adirondack type forming an intrusive mass and resulting from the differentiation of a noritic-anorthosite magma. The two variations of anorthosites noted are discussed.

INTRODUCTION

The writer has noted anorthosite occurrences near about Oddanchatram situated midway between Dindigul and Palni in Madurai district, during the field work undertaken in September. 1963, for his research and also for training the M. Sc. students in mapping. These rocks are found to be similar to the Kadavur anorthosites, which were for the first time recorded by Dr. A. P. Subramaniam, in 1956. Like the latter, the rocks under report are also of *Adirondack type and they may perhaps be correlated* with the Kadavur rocks. The area covered during the field work lies between the latitudes 10° 27′ and 10° 30′ and the longitudes 77° 40′ and 77° 52′, in the Survey of India Topo-sheets 58 F/11 and 58 F/15.

LOCATION OF ROCK EXPOSURES

Outcrops of anorthosites have been noted between the longitudes 77° 43′ and 77° 45′ and latitudes 10° 28′ and 10° 29′ in the Survey of India Topo-sheet No. 58 F/11. The locations of these outcrops are given below :

(1) *Kulandaivelappan malai, situated two miles west of Oddanchatram* ; a most important occurrence forming a large noritic gabbro-anorthosite massif.

(2) Ridge to the south of Oddanchatram Railway Station; mostly composed of noritic gabbros with anorthosites on its western flank.

(3) Minor outcrops to the north of Dindigul-Palni road on the western outskirts of Oddanchatram village.

It is quite likely that the soil covered intervening tract between the first two occurrences may be underlain by anorthositic rocks. This is revealed by a few specimens from well sections. The northward extension of these masses is indicated by the third exposure in the midst of cultivated fields.

GEOLOGICAL SETTING AND STRUCTURE

The area mapped shows the following sequence of rock types (vide map):

Soil cover and kankar;
Quartz veins and pegmatites;
Pink granites, pink and white aplites;
Acid and intermediate charnockites;
Noritic gabbros, anorthosites and monzodiorites;
Garnetiferous gneisses, sillimanite-garnet gneisses and migmatites.

The area between Rangaswamimalai on the west and Devarmalai on the east is suggestive of an anticlinal valley. The formations show a gradual veering of strike from N 60° E west of Puduchatram to N 65° W towards east. The dips are generally to NW on the western side and to NE on the eastern side, revealing the denuded assymetrical anticlinal structure with a plunge to NNE. Due to strong compressive shearing stresses, prominent conjugate jointing is developed in places particularly, in the basic members of the series. The valley is dotted by occasional low-lying relict ridges.

The anorthosite outcrops occur to the west of the above anticlinal structure. As the norite-anorthosite exposures are massive and devoid of any foliation and as these isolated outcrops are surrounded by cultivated lands, the structural features of this area are not quite clear. However, a careful and more detailed study (to be undertaken) may give some clues.

PETROLOGY

In the main occurrence of Kulandaivelappan malai massif, the following variations of rock types are noted in the field.

Charnockite – Noritic gabbro – Noritic anorthosite – Pure anorthosite – Garnetiferous anorthosite,

The Charnockites found on the eastern flank of the hill are coarse grained and yellowish gray and enclose mafic bands. The noritic gabbros are medium grained and rather dark coloured. The core of the mass is made up of pure anorthosite, light coloured and coarse grained. Further west are found the finer grained dark coloured garnetiferous anorthosites. Lenses and bands of noritic gabbro are found in the anorthosites. The rocks are generally massive and devoid of any foliation.

MINERALOGY AND PETROGRAPHY OF ANORTHOSITES

Two variations of anorthosites are found in the area under examination.

(1) PURE ANORTHOSITE

This is made up almost entirely of plagioclase with mafics restricted to a maximum of 5% hornblende. It is grayish and coarse grained. In hand specimens the plagioclase crystals occasionally show play of colours.

In thin section, the rock shows hypidiomorphic granular texture. Plagioclase feldspar is mostly subhedral and shows a protoclastic fabric by the presence of wedgeshaped and bent twin lamellae, undulose extinction, shattering and granulation.

The composition of the plagioclase has been determined by the universal stage method. It has an anorthite content of 55 – 60% and is hence of labradorite composition. The composition has also been found by Tatarsky's method by determining the R.I. values of $N'\gamma$ and $N'\alpha$ in fragments of random orientation. The R.I. values obtained by immersion method are $N'\gamma = 1.563$ and $N'\alpha = 1,558$. The result of this method is also $An_{56} \pm 3\%$.

The plagioclase grains sometimes show inclusions of dark rods arranged in parallel disposition, which is characteristic of labradorite.

The plagioclases are prominently twinned and some of the twin laws determined are albite, pericline and complex albite-Ala B.

The mineral shows alteration to calcite, chlorite, and muscovite in many grains.

Hornblende is the only mafic mineral of these rocks. It is subhedral to anhedral, and pleochroic from yellow to bluish green. It is

occasionally poikilitic with larger crystals of plagioclase. The mineral alters to calcite, chlorite and biotite. This mineral may have been derived from primary pyroxenes due to the action of late stage mineralizers. No residual pyroxene is found in eleven out of the twelve sections examined and only one section shows very litile diopside, partly altered to chlorite and amphibole. However, a few hornblende grains show the relict pyroxene cleavage.

(2) GARNETIFEROUS ANORTHOSITE

This is finer grained, dark coloured rock and characterized by the presence of garnet.

In thin section, it shows hypidiomorphic granular texture with plagioclase mostly in subhedral and garnet in anhedral grains.

In contrast to the first type, the plagioclase of this rock is relatively fresh without much alteration. Further, some grains are either untwinned or not prominently twinned. It is more calcic in composition with an anorthite content of 65 — 70 %and is thus of labratownite range It shows alteration to scapolite in a few grains.

The garnet is light brown in colour and is always anhedral and cuneiform. The presence of this mineral imparts a peculiar texture to the rock in thin section. It sometimes forms narrow rims around larger crystals of plagioclase giving the appearance of atoll garnet. Also, it encloses smaller grains of plagioclase. Amphibolization of the garnet is observed.

Hornblende is subhedral to anhedral and pleochroic from yellow to bluish green. It occurs both as an alteration mineral of garnet and as an independent constituent. It forms pseudomorphous rims after garnet around plagioclase. It also occurs as a synantectic mineral at the contacts of ore and plagioclase.

Scapolite occurs as an alteration mineral of plagioclase and is probably the result of later pneumatolytic effects. It is usually formed at the expense of untwinned plagioclase. It is surrounded by rims of garnet in a few places. The mean R. I. of scapolite has been found by immersion method and its composition determined from Shaw's determinative chart giving n_M versus % Me. The result obtained is as follows:

n_D = 1.560; composition 50 % Meionite. Ores and sphene are present as minor accessories.

ORIGIN

The origin of anorthosites is a much debated problem. Two types of anorthosite occurrences are recognized.

(*a*) Bytownite anorthosites which occur as major layered facies of great stratiform basic sheets or lopoliths. Examples: The Bushveld complex of S. Africa; the stillwater complex of Montana, U. S. A.

(*b*) Andesine–Labradorite anorthosites called the Adirondack type. These occur usually as intrusive masses of large or small areal extent with a domical structure. Examples: Anorthosite massifs of Adirondacks, N.Y.; Morin, Quebec; St. Paul, Labrador; Bergen and Egersund, Norway; Volhynia, U.S.S.R.

The first type is generally interpreted as resulting from the "sedimentary" accumulation of plagioclase crystals in basic magmas.

With regard to the origin of the second type, different points of view have been put forward.

Bowen, Balk and Barth hold that gravitative accumulation followed by filterpressing of the resultant crystalline differentiate can give rise to anorthosites of monomineralic composition. The associated granites, syenites represent the complementary residual liquids expelled during the operation. But they invoke different parent magmas—gabbroic, dioritic and granodioritic.

Buddington (1939) suggests that they have resulted from differentiation of a primary magma with the composition of a gabbroic anorthosite. This is supposed to have been formed by fusion and partial melting of the bytownite - anorthosite layer of the crust. In 1960, he suggested the possibility of the upward diffusing H_2O from the earth's interior causing the generation of a gabbroic anorthosite magma from the eclogite horizon.

Ramberg (1948) holds that they have been derived by metamorphic differentiation.

Metasomatic origin has been suggested for the anorthosites of Idaho by Hietanen (1956)

Michot (1955) in discussing certain anorthosites of Norway, has suggested a process called anorthositization of norites for the origin of those rocks.

A. P. Subramaniam (1956) has interpreted the Kadavur anorthosites as resulting from the intrusion of a magma of anorthositic composition and upheld the Buddington hypothesis.

Higgs (1954) has suggested that the San Gabriel anorthosite of Southern California was formed from a noritic or noritic anorthosite magma with 4 % water content at relatively low temperatures. He attributes the granulation and other protoclastic effects to explosive shattering due to concentration of water in the late stage residual magma. The release of confining pressure by some means leads to explosive expansion of water with consequent shattering of minerals. This process is called " Internal explosion shattering".

Pending a more detailed investigation, the following preliminary findings are given for the Oddanchatram anorthosites. They may be regarded as of Adirondack type representing an intrusive mass and resulting from the differentiation of a noritic anorthosite magma with a little H_2O content. The occurrence of nortic gabbros as border facies, the labradorite range of composition for plagioclase, the presence of mafic bands and lenses within anorthosites and the absence of any prominent layering in rocks are in support of this view. An important feature of these rocks is the presence of hornblende as the only mafic constituent to the nearly complete exclusion of pyroxenes. This may be ascribed to a process of autometamorphism brought about by the volatiles in the residual liquid The protoclastic effects observed may be explained by the phenomenon of " Internal explosion shattering " caused by the water originally present in the parent magma as suggested by Higgs.

In the garnetiferous anorthosite, the mode of occurrence of garnet, as revealed by microscopic study suggests the possibility of this mineral being of primary origin. There is no indication of its formation as a reaction mineral. Hence this rock may be regarded as resulting from the local development of a magma with those constituents. The earlier crystallized plagioclase may have sunk into the underlying melt of garnet composition seperated by liquid immiscibility. The garnet solidified later in the interstitial spaces between plagioclase crystals as anhedral grains.

The noritic gabbros associated with anorthosites represent the complementary differentiates of the noritic anorthosite magma. The question whether the associated charnockites have got any genetic relationship with the anorthosites is yet to be studied.

Further work on the rocks discussed in this paper is under progress.

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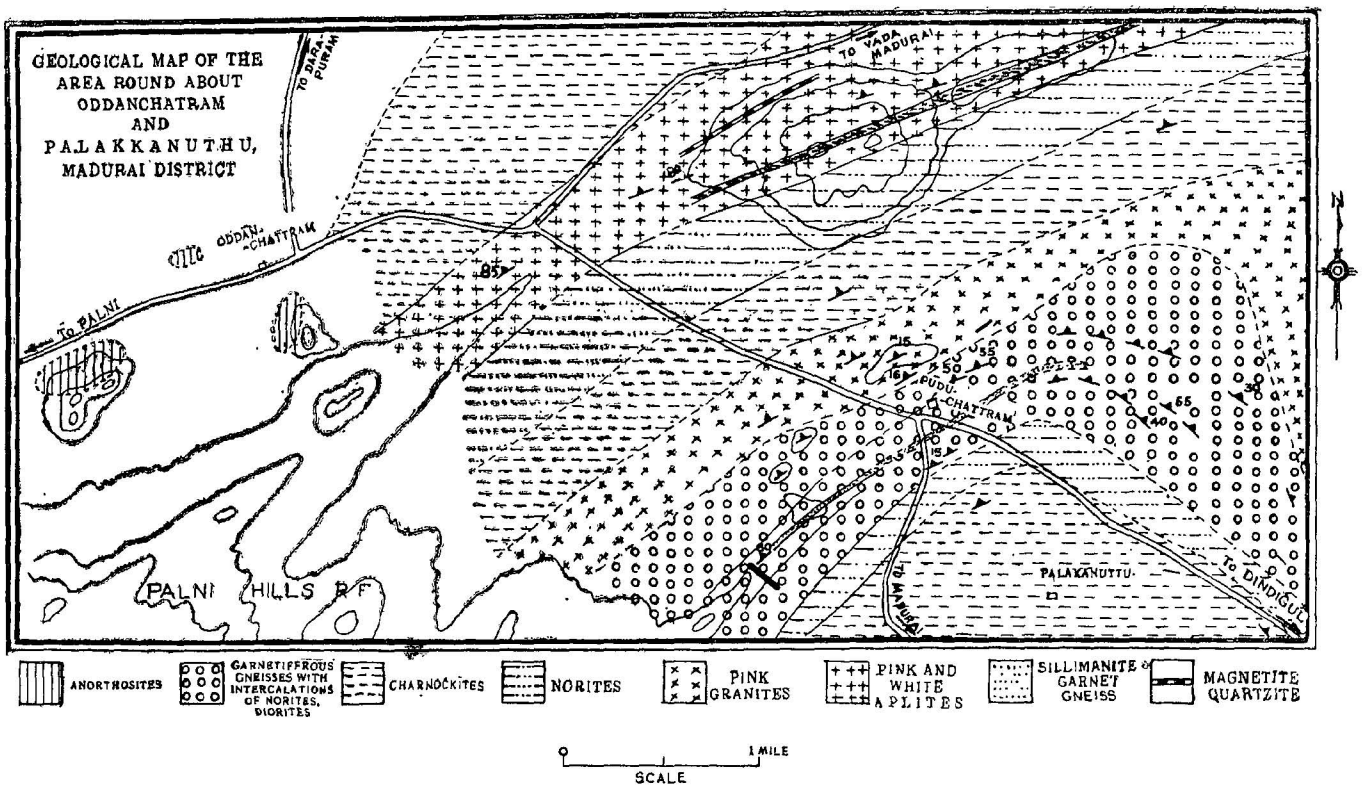
GEOLOGICAL MAP OF THE AREA ROUND ABOUT ODDANCHATRAM AND PALAKKANUTHU, MADURAI DISTRICT
TO DARAPURAM
TO VADA MADURAI
ODDAN-CHATTRAM
TO PALNI
PUDU-CHATTRAM
PALAKANUTTU
TO DINDIGUL
TO MADURAI
PALNI HILLS RF
ANORTHOSITES
GARNETIFEROUS GNEISSES WITH INTERCALATIONS OF NORITES, DIORITES
CHARNOCKITES
NORITES
PINK GRANITES
PINK AND WHITE APLITES
SILLIMANITE GARNET GNEISS
MAGNETITE QUARTZITE
1 MILE
SCALE

THE STRUCTURE OF SIVAMALAI SYENITE COMPLEX — A NOTE

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Sivamalai (11°2′ : 77°33′) in Coimbatore district is well known as a nepheline-syenite area. This has been studied by C. S. Middlemiss in 1896 and by T. H. Holland in 1901. During 1941 A. P. Subramaniam now of the Geological Survey of India had taken Sivamalai Syenites for his M. Sc. Study : the next report (1951) on the area could be obtained from an unpublished M. Sc. thesis of T. S. Nagasundaram, a research scholar under Professor T. N. Muthuswami.

It wonld perhaps be true to say that the structural aspects of this complex have not engaged the attention of the earlier workers. It cannot be otherwise because field tectonic studies have considerably improved in modern times.

This short paper sets forth the structural features of the Sivamalai Syenite complex. As the map indicates, the syenites of the main hillock of Sivamalai should be considered as by far the largest exposure, which to its west shows a number of outcrops detached one from the other, with a general E.N.E.–W.S.W. trend. It looks fairly clear, that the main mass with a trend nearly east to west had been subjected to repeated faulting bringing in its wake the displacements as now observed. That the faulting movement had taken a diagonal trend finds its evidence in the lineation of the fault groove taken in the gneiss north of 1087 hill. The lineation trends N. 14° E with a plunge of 32° towards north.

It is interesting to observe that the faulting is a result of cross-folding. Although the effects of cross-folding could not be clearly traced in the faulted zone, evidence for the same is indicated in the gneiss and pyroxene granulites which are associated with the nepheline syenites. The cross-fold axis trends in the same N. E. - S. W. direction as the fault plane.

The cross-folds had resulted due to the secondary stress movements acting on the original major plunging fold. A clue to this is obtained in the drag-folded and faulted banded ferruginous quartzites – the marker horizons – that outcrop between Sadayampuram and Illiyamputtur. The lineation of the drag-fold has a trend N. 10° W plunging 67° towards north. It should of course be granted that this trend should have been modified to some extent by the secondary stress movements of the cross-folding period.

From the foregoing observations, it would be clear that the intrusion of the syenite masses has followed the first phase of the major plunging fold and has been later affected by the secondary stresses that gave rise to cross-folding and faulting.

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I am thankful to Professor T. N. Muthuswami for helpful criticism and valuable guidance in the preparation of this short paper.

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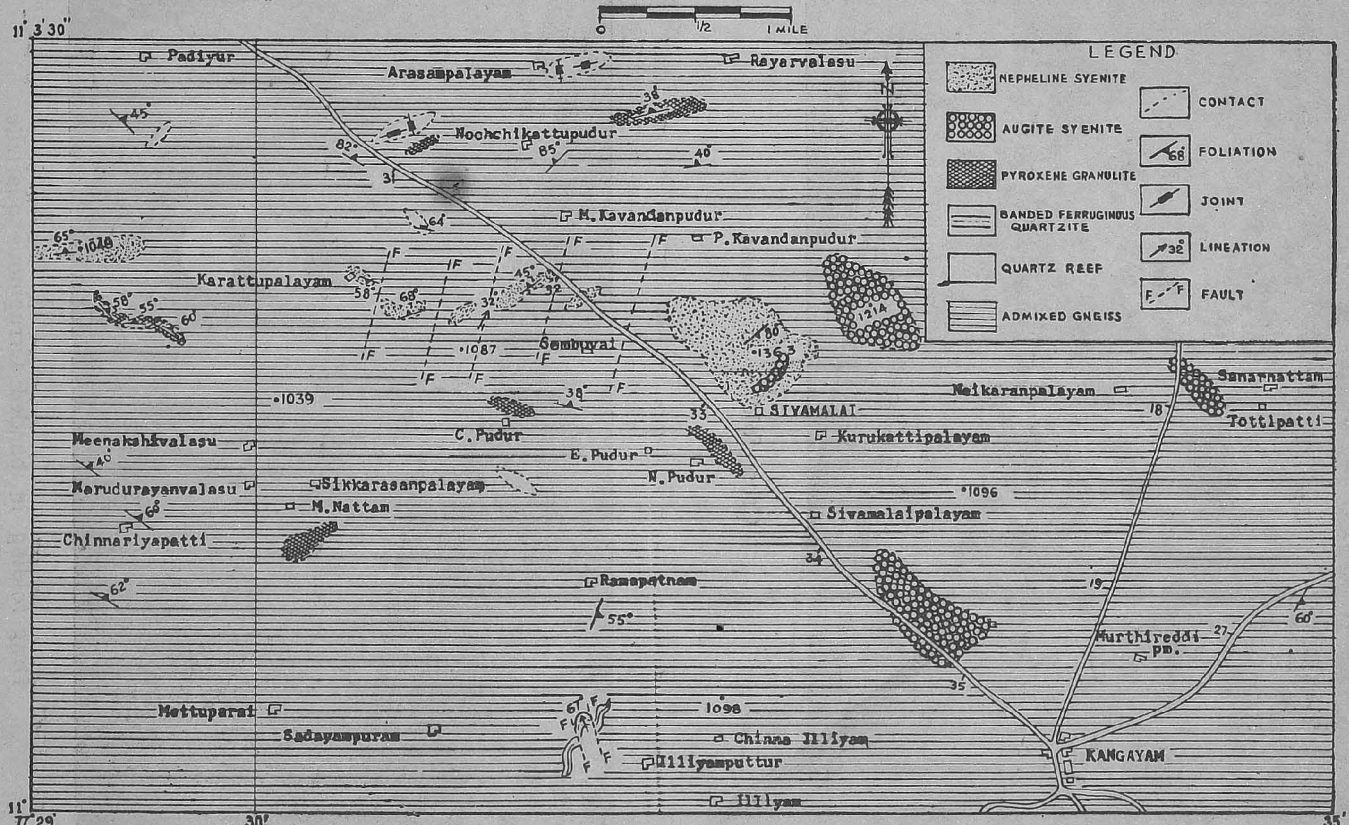
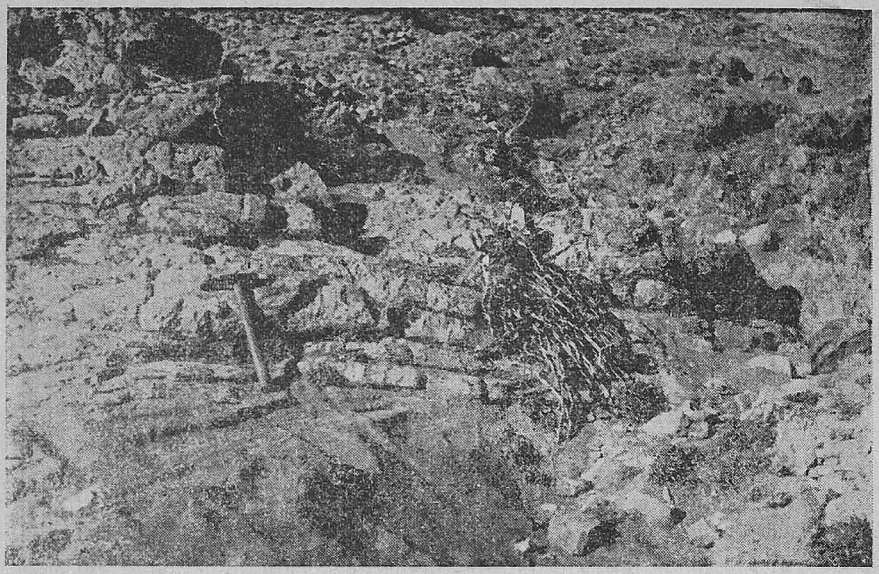
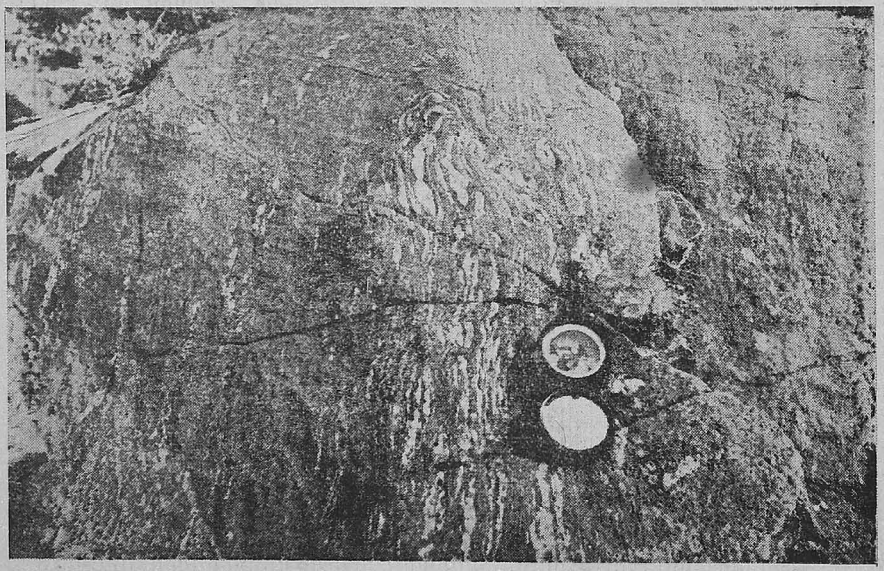
GEOLOGICAL MAP OF SIVAMALAI AND NEIGHBOURHOOD





Cross-folding in gneiss



Drag-folding in banded ferruginous quartzite.

STUDIES IN THE ECOLOGY OF THE VELLAR ESTUARY
3. THE INTERTIDAL AND ESTUARINE POLYCHAETA

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U. G. C. Centre for Advanced Training
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Introduction

Southern (1921) studied the Polychaeta from the Chilka Lake and also from the brackish waters of other parts of India. Panikkar and Aiyar (1937 & '39) have recorded observations on polychaete fauna in their faunal investigations of brackish waters around Madras. Very little work has been carried out on the brackish water and estuarine fauna of the other areas in India. This paper is only a preliminary account of the systematic collections made periodically from the intertidal areas of the sea and Vellar estuary at Portonovo. The collections were made by digging with a shovel in the intertidal areas and by dredging with a Petersen dredge in the estuary and by passing the material through a seive. The hydrographical characteristics of the Vellar estuary, especially the salinity and temperature conditions, have been described by Jacob and Rangarajan (1962) and they found that the mixing and circulation in the Vellar estuary is similar to the atidal esturies of the southwest Australia in general and to the Swan River system in particular (Rochford, 1951). The semi-quantitative scheme of Endean, Kenny and Stephenson (1956) has been adopted in the present study.

Distribution

In an earlier paper (Balasubrahmanyan, 1960a) I have listed twenty species of polychaetes to be occurring in the bottom at various places of the Vellar estuary. A total of twentynine species have been so far collected in the Vellar estuary and from the intertidal area of the sea shore at Portonovo (Table 1).

Leanira japonica and *Hesione intertexta* were collected form the logs of wood washed ashore near the mouth of the Vellar estuary. In the estuary *Mercierella enigmatica* was found to colonise the submerged piles, rocks and dead shells during the summer months (April to June). *Tomopteris*

elegans was occasionally found to occur in the estuarine plankton during the summer months. Only four species *Onuphis eremita*, *Nerine cirratulus*, *Glycera alba* and *Pisionidens indica* were collected from the intertidal area of the sandy beach at Portonovo. *Onuphis eremita* was never found to occur in the estuary.

Marphysa gravelyi and *Mastobranchus indicus* were collected from the intertidal areas of the Vellar estuary only, while *Dendronereis aestuarina* and *Diopatra neapolitana* present similarly in the intertidal area, were found to a depth of one meter only in the estuary. *Tylonereis fauveli*, *Heteromastus similis*, *Branchiocapitella singularis*, *Paraheteromastus tenuis*, *Lycastis indica*, *Nerine cirratulus* and *Glycera alba* collected from the intertidal area of the estuary were found to be present at various depths in the Vellar estuary (Balasubrahmanyan, 1960a). *Glycera alba* and *Nerine cirratulus* alone were found to be present in the intertidal areas of the estuary and sea shore and also at various depths in the estuary. *Pisionidens indica* present in the intertidal area of the seashore was also found at the bottom near the mouth of the Vellar estuary.

Cossura delta, *Ancistrosyllis constricta*, *Nerine chilkensis*, *Nephthys polybranchia*, *Lumbriconereis polydesma*, *Lumbriconereis simplex*, *Euclymene annandalei*, *Spio bengalensis*, *Prionospio polybranchiata*, *Pectinaria crassa* and *Laonome indica* were collected from the bottom and not in the intertidal area of the Vellar estuary. *Nerine cirratulus* was found to be a dominant form in the intertidal area of the sea shore, while *Diopatra neapolitana* was the dominant form in the intertidal area of the Vellar estuary upto a distance of one kilometer from the mouth. As reported earlier (Balasubrahmanyan, 1960b) *Cossura delta* was found to be dominant in a limited area of the Vellar estuary at a depth of two to four meters.

Summary

The paper is a preliminary report of the polychaetes collected periodically from the intertidal areas of the estuary and sea shore and also at different depths in the estuary. A total of twentynine species have been so far collected from the sea shore and in the estuary.

Nerine cirratulus and *Diopatra neapolitana* were found to be the dominant forms respectively in the intertidal area of the sea shore and estuary while *Cossura delta* was the dominant form at a depth of two to four meters in the estuary.

Acknowledgements

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	1960b	*Cossura delta* Reish (Polychaeta) from the Vellar estuary. *J. Mar. biol. Ass. India*, II, 264—265.
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TABLE I.

List of Intertidal and Estuarine Polychaetes.

Species	Distribution	Ecological significance
Leanira japonica McIntosh	crevices in wood	Present
Pisionidens indica Alikunhi	intertidal&benthic	,,
Hesione intertexta Grube	crevices in wood	,,
Ancistrosyllis constricta Southern	benthic	Common
Tomopterosyllis elegans Chum	plankton	Present
Lycastis indica Southern	intertidal&benthic	,,
Tylonereis fauveli Southern	–do–	,,
Dendrnereis aestuarina Southern	–do–	,,
Nereis chilkensis Southern	benthic	,,
Nephthys polybranchia Southern	benthic	Common
Marphysa gravelyi Southern	intertidal	Present
Diopatra neapolitana Della Chiaje	intertidal&benthic	Dominant
Onuphis eremita Audouin&M-Edwards	intertidal	Present
Lumbriconereis polydesma Southern	benthic	Common
Lumbriconereis simplex Southern	benthic	Present
Glycera alba Rathke	intertidal&benthic	Present
Nerine cirratulus Della Chiaje	–do–	Dimonant
Spio bengalensis Willey	benthic	Present
Prionospio polybranchiata Fauvel	benthic	Present
Cossura delta Reish	benthic	Dominant
Ammotrypane aulogaster Rathke	benthic	Present
Heteromastus similis Southern	intertidal&benthic	Common
Paraheteromastus tenuis Monro	–do–	,,
Mastobranchus indicus Southern	intertidal	,,
Branchiocapitella singularis Fauvel	intertidal&benthic	,,
Clymene (Euclymene) annandalei Southern	benthic	Present
Pectinaria (Amphictene) crassa Gruba	–do–	,,
Laonome indica Southern	–do–	,,
Mercierella enigmatica Fauvel	Fouling	Common

FREE HISTIDINE IN SOME FISH TISSUES

By

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The nitrogenous extractives play an important role in the intermediate protein metabolism. Their study in various animal types has proved to be one of the interesting chapters in the history of biochemistry. In fish muscle the nitrogenous extractives form a relatively small proportion of total nitrogen and contribute little to the value of the fish, but are important in other ways. Some of the nitrogenous extractives have been regarded to be contributory causes for the flavour of the fish. The relative keeping quality of the various species is dependent on the ease with which the nitrogenous extractives are attacked by micro organisms. The nature and amount of the decomposition products of these nitrogenous extractives may determine whether the fish is edible or not, or even whether it is poisonous or not. Kimata (1941) has shown that the speed of decomposition of various species is dependent almost wholly on the nature of the nitrogenous extractives, the muscle proteins being attacked at approximately the same rate.

The nitrogenous extractives of some of the common fish have been under investigation as a part of the study of their nitrogen metabolism. The present account deals with the free imidazole derivative, histidine. We know little regarding the role of free histidine in tissues. Some investigators have suggested for it a buffering role and others a metabolic role. Apart from this, histidine is important in another way. By decarboxylation it can give rise to histamine, which is toxic.

Airam and Power (1952) determined the histidine content in some of the fresh water fishes aud found wide variations. Wood *et al* (1960) have recently studied the free histidine content of the tissues in Sockeye salmon during spawning migration. In the present account the histidine content in the fresh muscle tissue was investigated in eleven species of teleots, viz.

1. *Tilapia mossambica* (Peters) 2. *Arius malabaricus* 3. *Mugil dussumieri* (Val) 4. *Mugil cephalus* Linn. 5. *Mugil spieigleri* 6. *Thrissocles*.

malabaricus 7. *Polynemus tetradactylus* (shaw) 8. *Opisthopterus tardoore* (Cuv) 9. *Hilsa toli* (Cuv.) 10. *Ophiocephalus striatus* Block 11. *Dussumiera acuta* (Cuv. & Vol.)

The histidine content in red and white muscles was determined in *Arius malabaricus* and *Dusseumieria acuta*. The effect of spoilage at different temperature on the free histidine content of muscle tissue was determined in *Hilsa toli* (Cuv.) and *Thrissocles malabaricus*, and the free histidine content in different tissues was investigated in *Arius malabaricus*.

Analytical Procedure

Fresh material was invariably used for determination of free histidine except in the study of the effect of spoilage. Extracts were prepared in accordance with the procedure described by Wood, Duncan and Jackson (1960). The muscle was extracted five times with alcohol. Determination was done mainly by the method described by Chattaway (1947). However the method described by Wood *et al* (1960) was also tried. The results from the two procedures did not differ, but as the method described by Chattaway (1947) was less time-consuming, it was adopted.

The mean values and the range of variation of four separate determinations on each sample of tissue are presented in the results.

Observations

The results of the analyses are shown in Tables I to IV. It will be seen from Table I that the content of histidine varies from 53 to 204 mg/100g in the muscle of the different species investigated.

Table I

Showing histidine content of the muscle of different teleosts. The values represent the mean of four separate estimations.

	mg/100g wet tissue
1. *Tilapia mossambica*	53.6 (51.0–55.7)
2. *Arius Malabaricus*	194.4 (188–195.9)
3. *Mugil dussumieri*	70.0 (68.4–71.9)

4.	*M. Cephalus*	76.50 (74.0–72.8)
5.	*M. Speigleri*	71.40 (69.0–77.0)
6.	*Thrissocles malabaricus*	57.60 (56.0–58.9)
7.	*Polynemus tetradactylus*	50.00 (45.8–51.0)
8.	*Ophisthoptcrus tardoore*	54.01 (52.8–56.9)
9.	*Hilsa toli*	55.90 (50.8–56.8)
10.	*Ophiocephalus striatus*	54.01 (52.0–56.8)
11.	*Dussumieria acuta*	204.0 (201.2–206.0)

From Table II given below it will be seen that the red muscle in both the species studied contains a higher percentage of free histidine.

Table II

Histidine content of Red and white muscle. (Mean values for four determinations.)

Species	Red mg/100g	White mg/100g
Dussemieria acuta	204.0 (200.3–205.9)	141.0 (140.0–143.0)
Arius malabaricus	200.0 (186.0–204.0)	184.0 (178.0–185.2)

Showing histidine content is greater during spoilage at higher temperature as shown in Table III.

Table III

Histidine content during spoilage at different temperatures.

	Fresh	Spoilage at Room temp. (8 hours)	Spoilage at 40°c (8 hours)

Thrissocles malabaricus	57.6	68 9	84.7
	(55.0–59.2)	(66.4–69.2)	(81.2–86.1)
Hilsa tolt	55.9	65.0	86.0
	(53.2–56.7)	(64.8–67.9)	(84.7–88.0)

With regard to the distribution of histidine in the different tissues of *Arius*, it is found that the heart tissue has a higher content of histidine as shown below.

Table IV

Histidine content of different tissues of *Arius malabaricus*
(Mean values for three determinations)

Tissue	mg/100g wet tissue
Liver	13.2
	(11.0–14.2)
Kidney	21.6
	(20.0–23.4)
Intestine	48.1
	(47.8–49.9)
Stomach	44.4
	(42.4–45.0)
Heart	166.0
	(159.0–168.0)

In view of the limited knowledge we have of the content and distribution of free histidine in fish tissues, it is difficult to give a comparative survey. Airam and Power (1952) have reported wide variations in the histidine content of the fresh water fishes. Some species had high content, some very low. It has also been reported that Singapore fishes in general showed a high content of histidine (Geiger and Borgstrom 1962.) Histidine is in a sense a unique constituent, as it may be entirely absent or low, or high in different species. The significance of this variation in histidine content and the formation of histamine in some of the economically important species is under investigation. The histidine-histamine metabolic pathway is little understood so far.

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ON A REGRESSION MODEL FOR CHARACTERISTICS OF SECONDARY SCHOOL STUDENTS

By

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In a previous investigation*, a sample survey was conducted among the higher secondary school students, with a view to discriminate the urban and rural charactor of the students. A student was considered to belong to 'urban' class if his native place was urban; in the alternative case the student was classified as 'rural'.

The observed characteristics for the students of each category were, the weight 'W' in pounds, the age 'A' in years, the height 'H' in inches and the chest girth 'C' in inches. The above characteristics were observed for a sample of 476 students of 'rural' category and 162 students for 'urban' category. In this note we use the same terminology as in the previous investigation and the data collected for the previous analysis are utilised for framing regression equations and for deriving certain other connected results.

The interesting conclusion arrived in this note is that the two regression equations for 'W' in terms of 'A', 'H' and 'C', for the rural and urban groups are not significantly different in the statistical sense.

The following results will be used for the investigations in this note.

		Rural	*Urban*
	Sample size	476	162
Means.	Weight	83.27	80.85
	Age	15.595	15.222
	Height	60.05	59.54
	Chest Girth	28.5	28.07

* Sample survey conducted by the author in connection with his M. Sc. thesis (1963)

		Rural	*Urban*
Corrected sums of squares and products.	S_{WW}	115884.50	33266.44
	S_{AA}	1168.75	404.00
	S_{HH}	8157.68	2198.28
	S_{CC}	3153.00	817.11
	S_{WA}	6644.71	2062.33
	S_{WH}	22480.17	6593.89
	S_{WC}	14366.00	3806.78
	S_{AH}	1412.14	461.67
	S_{AC}	876.50	234.33
	S_{HC}	2995.50	794.56

Adopting the regression model,

$$W = \alpha + \beta_1 A + \beta_2 H + \beta_3 C$$

where α, β_1, β_2, β_3 are to be estimated by the method of least squares, the regression equation for 'rural native place' is found to be

$$W = -109.45 + 1.958\ A + 1.449\ H + 2.635\ C \quad \ldots \quad (1)$$

and the regression equation for 'urban native place', is

$$W = -118.46 + 1.663\ A + 1.756\ H + 2.474\ C \quad \ldots \quad \ldots \quad (2)$$

To test whether the concommitant variables in the regression equations are useful in the prediction of weight, the hypothesis $\beta_1 = \beta_2 = \beta_3 = 0$, is tested in both the classes. Tables No. 1 and 2 furnish the required data.

TABLE No. 1

Test of the hypothesis $\beta_1 = \beta_2 = \beta_3 = 0$ for 'rural class'

Source	D. F.	S. S.	M. S. S.	'F'
Regression	3	83438.521	27812.84	404.6***
Residual	472	32445.975	68.74	
Total	475	115884.496		

TABLE No. 2

Test of hopothesis: $\beta_1 = \beta_2 = \beta_3 = 0$ for 'urban class'.

Source	D. F.	S. S.	M. S. S.	'F'
Regression	3	24426.39	7341.29	131.81***
Residual	158	8800.05	55.7	
Total	161	33226.44		

The variance ratios are significant in both the cases at 0.1 per cent level even, showing that the variables considered above are decidedly useful in prediction.

It is now to be examined whether the three linear dimensions are of equal importance in the prediction formula. From the set of estimates of α's and β's it is seen that the coefficient b_3 for chest girth for both the groups is greater than the other two coefficients. The hypothesis relevant to examine at this juncture is $\beta_1 = \beta_2 = \beta_3 = \beta$ and the following tables furnish the analysis of the sum of squares for both the cases.

TABLE No. 3

Test of the hypothesis: $\beta_1 = \beta_2 = \beta_3 = \beta$ for the 'rural class'.

Source	D. F.	S. S.	M. S. S.	'F'
Deviation from equality	2	1371.23	685.61	9.7***
Residual	472	32445.97	68.74	
Total	474	33817.20		

TABLE No. 4

Test of the hypothesis: $\beta_1 = \beta_2 = \beta_3 = \beta$ for the 'urban class'.

Source	D. F.	S. S.	M. S. S.	'F'
Deviation from equality	2	158.44	79.22	1.423
Residual	158	8800.05	55.70	
Total	160	8958.49		

The 'F' ratios are significant and so there is no evidence from the data to conclude that $\beta_1 = \beta_2 = \beta_3$ are same for both the categories.

As we have to compare the rural and urban character of students it is necessary to test whether the regression functions constructed for the two series (Equations (1) and (2) given in the beginning) are same. Following the method suggested by C. R. Rao, the residual sum of squares is $R_0^2 = 41246.026$.

The two samples are thrown together and considered as a single sample of size $(n + n')$ and the regression equation is determined and the new regression coefficients are $B_1 = 1.895$; $B_2 = 1.512$ and $B_3 = 2.603$.

The analysis of variance test for this is given below.

TABLE No. 5

Analysis of variance for testing equality of regression coefficients.

Residual due to	D. F.	S. S.	M. S. S.	'F'
Deviation from hypothesis	4	68.007	17.002	0.2597
Separate regressions	630	R_0^2 41246.026	65.470	
Total	634	R_1^2 41314.033		

The calculated 'F' ratio is not at all significant and so there is no evidence from the data to conclude that the regression functions are different.

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FORCE CONSTANTS, ROTATIONAL DISTORTION CONSTANTS AND THERMODYNAMIC PROPERTIES OF THIO-CARBONYL FLUORIDE

by

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Abstract:

A normal coordinate analysis for SCF_2 molecule belonging to C_{2v} point group have been carried out using Wilson's F. G. Matrix method. The potential energy constants obtained in this case have been made use to calculate the rotational distortion constants on the basis of the first order perturbation theory of Kivelson and Wilson. The molar thermodynamic properties for SCF_2 molecule for 11 temperatures from 100 to 1000°K for the ideal gaseous state at one atmospheric pressure and with the usual rigid-rotor harmonic oscillator approximation have also been calculated.

Introduction :

The infrared spectrum of the molecule SCF_2, in the range 300–4000cm^{-1} has been studied by Downs[1] and he assigned the observed frequencies on the basis of C_{2v} symmetry. Only very few molecules having S = C bond have been subjected to normal coordinate analysis. As such it is thought worthwhile to carry out such an analysis for this molecule and the results obtained are reported here.

Normal coordinate analysis:

Molecules of the XYZ_2 type belonging to C_{2v} symmetry have six fundamental vibrations. Of these six vibrations 3 belong to the totally symmetric a_1 species. The remaining three, are antisymmetric species, two of b_1 type and one of b_2 type. The symmetry coordinates and the G matrix elements used here are the same as reported by Venkateswarlu and Sundaram[2] excepting the G matrix element G_{66} corresponding to the out of plane

vibration. The correct expression for G_{66} as given by Krishna Pillai and Cleveland[3], is

$$G_{66} = \mu_X \left[1/D^2 + \frac{1}{d^2 \cos^2 \mathcal{L}/2} + \frac{2}{Dd \cos \mathcal{L}/2}\right] + \mu_Y/D^2 + \frac{\mu_Z}{2\ d^2 \cos^2 \mathcal{L}/2}$$

where μ_X, μ_Y and μ_Z are respectively the reciprocals of the masses of the atoms X, Y and Z. D and d are respectively, the X–Y and X–Z internuclear distance and $\mathcal{L}$ is the Z–X–Z interbond angle.

Precise knowledge of the structural parameters of this molecule either from Microwave or Electron Diffraction studies is lacking. As such the C = S and C — F bonds are assumed to be 1.56 and 1.32°A respectively and the F — C — F angle is taken as 112°30′ These assumption are based on the structural parameters of carbonyl fluoride[4] and carbonyl sulphide[5] molecules.

The secular equations were solved in the usual way to obtain the symmetry force constants (F). The valence force constants (f) obtained there from are given in Table I. The frequencies computed making use of these constants agree very well with the observed frequencies as may be seen from Table II

TABLE I

FORCE CONSTANTS FOR SCF_2 MOLECULE IN md/A° *

Bond stretching and bond interaction constants.	Angle bending and angle angle interaction constants.	Bond–angle interaction constants.
f_D = 6.9000	$f_{\mathcal{L}}$ = 1.0300	$f_{d\mathcal{L}}$ = 0.1250
f_d = 6.2500	f_β = 0.5364	$f_{d\beta}$ = 0.4739
f_{Dd} = 1.0182	$f_{\beta\beta}$ = 0.1090	$f_{d\mathcal{L}}$ = –0.726
f_{dd} = 0.6500	f_δ = 0.3301	$f_{D\beta}$ = 0.2069
	$f_{\mathcal{L}\beta}$ = 0.0874	

* D refers to C = S bond, d to S–F bond, $\mathcal{L}$ and β refer to F—$\hat{C}$—F and F—$\hat{C}$—S respectively; γ = angle between the X—Y bond and ZXZ plane.

TABLE II

CALCULATED AND OBSERVED FREQUENCIES FOR THE SCF_2 MOLECULE

Frequency symbol	Wave numbers in Cys/cm.	
	Calculated	Observed
$\nu_1(a_1)$	782.0	787.0
$\nu_2(a_1)$	1379.0	1368.0
$\nu_3(a_1)$	522.0	526.0
$\nu_4(b_1)$	1203.0	1189.0
$\nu_5(b_1)$	412.0	417.0
$\nu_6(b_2)$	622.0	622.0

The value of C = S stretching constant 6.9 is very nearly the same value (i. e. 6.8) for C = S stretching force in this carbonyl chloride molecule[2]. C–F stretching force is also comparable with the value of C–F stretching force for carbonyl fluoride[3].

Rotational Distortion constants:

Kivelson and Wilson[6] have given general methods for deriving expressions for the rotational distortion constants as functions of the atomic masses, internuclear distances interbond angles and the elements of the inverse potential energy matrix F^{-1}.

The expressions used in the present work for the quantities $\left[J^{i}_{\alpha\beta} \right]$, which are the derivatives (evaluated at the origin) of the elements of moment of inertia tensor with respect to the symmetry co-ordinates (α, β, γ or δ = x or y or z), were taken from the results of Krishna Pillai and Cleveland[3] for XYZ_2 type molecules. Using J's and the f's in Table I, the rotational distortion constants given in Table III were obtained.

TABLE III

ROTATION DISTORTION CONSTANTS FOR SCF_2 MOLECULE IN KC/Sec.

Constants	Calculated value for SCF_2
D_J	1.00023
D_K	7.05869
D_{JK}	8.17136
R_5	-1.64398
R_6	-0.06770
δ_j	0.34386

Thermodynamic properties:

Using the observed frequencies given in Table II thermodynamic properties (of the molecule) such as heat content, free energy, entropy and heat capacity for this molecule for 11 temperatures from 100 to 1000°K are calculated and are tabulated here.

TABLE IV

HEAT CONTENT H°, FREE ENERGY F°, ENTROPY S° AND HEAT CAPACITY Cp° FOR THE IDEAL GASEOUS STATE AT ONE ATMOSPHERIC PRESSURE *

Temperature T	$H°—E°_0$	$-F_0—E°/T$	S°	Cp°
100	7.9851	42.5051	50.4909	8.2047
200	8.5802	48.1838	56.7640	10.3379
273.16	9.2803	50.9621	60.2423	12.0336
300	9.5563	51.8432	61.3986	12.6025
400	10.5444	54.7291	65.2742	14.3552
500	11.4462	57.1832	68.6294	15.6487
600	12.2303	59.3390	71.5652	16.5849
700	12.8980	61.2689	74.1669	17.2681
800	13.4717	63.0251	76.4968	17.7666
900	13.9763	64.6481	78.6245	18.1474
1000	14.4125	66.1405	80.5410	18.4369

* T is the temperature in degrees Kelvin, the other quantities are Cal. deg^{-1} mol^{-1} and $E°_0$ is the energy of one mole of perfect gas at absolute zero.

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POTENTIAL ENERGY CONSTANTS AND THERMODYNAMIC PROPERTIES OF SOME TERTIARY BUTYL HALIDES

BY

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ABSTRACT

Using the Wilson F-G matrix method, the potential energy constants of $(CH_3)_3CCl$, $(CH_3)_3CBr$ and $(CH_3)_3CI$ have been calculated. The observed vibrational frequencies are utilised to calculate the molar thermodynamic functions of the above molecules for ll temperatures between 100^0 and 1000^0 K to a rigid rotor, harmonic, oscillator, ideal gas approximation.

POTENTIAL ENERGY CONSTANTS

In the present investigation, a normal co-ordinate analysis has been carried out for the molecules $(CH_3)_3CCl$, $(CH_3)_3CBr$ and $(CH_3)_3CI$ using the Wilson F-G Matrix method[1, 2] As a first approximation, the (CH_3) groups are considered to be point masses. In such a case the F and G matrix elements will be identical to that for the XY_3Z type of molecules. The orthonormal set of symmetry co-ordinates and the elements of the kinetic energy matrix used in this investigation are the same as those obtained by Meister and Cleveland[3]. The elements of the potential energy matrices have been obtained by the authors using a most general quadratic potential function. Making use of the vibrational frequencies of these molecules reported by Kohlrausch[4] and the molecular parameters obtained by Williams and Gordy[5], Beach and Stevenson[6] and Dornte,[7] the force constants are evaluated in the usal way and are given in Table I. The observed frequencies and the frequencies obtained by solving the secular equations are given in Table II. They are found to be in good agreement.

From the results given in Table I, it may be seen that the C–Cl, C–Br and C–I stretching constants are in the decreasing order while the C–(CH_3) stretching constant is almost the same in all three cases. The

(CH_3)-C-(CH_3) and (CH_3)-C-X bending constants also are nearly equal in all the cases while the interaction constant f_{Dd} between the bonds C-X and C-(CH_3) is in the decreasing order. Here X stands for the halogen atom.

TABLE I

Potential Enery Constants of $(CH_3)_3CCl$, $(CH_3)_3CBr$ and $(CH_3)_3CI$ in 10^5 dynes/Cm.

Potential Constants	$(CH_3)_3CCl$	$(H_3)_3CBr$	$(CH_3)_3CI$
f_D	3.855	3.325	2.823
f_d	4.861	4.826	4.761
f_{dd}	0.783	0.748	0.689
$f_{\mathcal{L}}$-$f_{\mathcal{L}\mathcal{L}}$	0.562	0.544	0.501
f_{β} -$f_{\beta\beta}$	0.601	0.583	0.570
$f_{d\mathcal{L}}$	0.482	0.473	0.469
$f_{d\beta}$	0.491	0.484	0.476
$f_{\mathcal{L}\beta}$	0.374	0.367	0.356
f_{Dd}	0.518	0.391	0.329
$f_{D\mathcal{L}}$—$f_{D\beta}$	-0.968	-0.850	-0.777

D=C-X bond length; d=C-CH_3 bond length:
$\mathcal{L}$=CH_3-C-CH_3 angle; β=CH_3-C-X angle;
Here X stands for the Halogen Atom.

TABLE II

Observed and Calculated Frequencies.

Species	$(CH_3)_3CCl$		$(CH_3)_3CBr$		$(CH_3)_3CI$	
	Observed	Calculated	Observed	Calculated	Observed	Calculated
	372	373	303	303	259	259
a_1	570	573	515	514	487	488
	812	818	805	809	801	806
	304	302	268	269	227	230
e	406	408	398	397	386	390
	925	930	932	940	927	933

THERMODYNAMIC PROPERTIES

The heat content, free energy, entropy and heat capacity of the above three molecules are calculated for 11 different temperatures from 100° to 1000° K making use of the observed fundamental frequencies. A rigid rotor, Harmonic oscillator approximation is assumed and the values are calculated for the ideal gaseous state at one atmospheric pressure. The nuclear spins and isotropic mixing are neglected. The moments of Inertia were calculated using the structural parameters of Williams /et al,[5] Beach[6] and Dornte[7]. The symmetry number is 3. The Thermodynamic properties of $(CH_3)_3CCl$, $(CH_3)_3CBr$ and $(CH_3)_3CI$ thus obtained are listed in Tables III, IV and V.

TABLE III

Thermodynamic properties of $(CH_3)_3CCl$ for the ideal gaseous state at one atmospheric pressure*

T° (K)	$\frac{H_o - E^\circ_0}{T}$	$-\frac{F^\circ - E^\circ_0}{T}$	S°	C°_p
100	8.297	46.876	55.173	9.262
200	10.351	53.205	63.555	15.046
273.16	12.182	56.703	68.885	19.172
300	12.900	58.310	71.110	20.720
400	15.486	61.930	77.417	25.868
500	18.044	65.673	83.717	30.374
600	20.414	69.190	89.604	34.003
700	22.562	72.484	95.046	36.977
800	24.533	75.627	100.172	39.491
900	26.339	78.621	104.960	41.612
1000	27.927	81.489	109.416	43.429

*H_0 = Heat Content; F° = Free Energy; S° = Entropy. C°_p = Heat Capacity at Constant Pressure; T = Temperature in degree Kelvin; E°_o = Energy per gram molecule of the perfect gas at T = 0° K and all the quantities are in cal. Deg^{-1}. $Mole.^{-1}$

TABLE IV

Thermodynamic properties of $(CH_3)_3CBr$ for the ideal gaseous state at one atmospheric presure.

T° (K)	$\frac{H_0 - E_0^\circ}{T}$	=	$\frac{F^\circ - E_0^\circ}{T}$	S°	C_p°
100	8.472		48.881	57.353	10.238
200	10.783		55.425	66.208	15.773
273.16	12.635		59.061	71.696	19.631
300	13.332		60.278	73.610	21.076
400	15.760		64.268	80.026	26.064
500	18.396		68.299	86.700	30.544
600	20.753		71.874	92.626	34.118
700	22.844		75.176	98.020	37.048
800	24.798		78.386	103.186	39.562
900	25.470		81.272	107.741	41.599
1000	28.172		84.307	112.473	43.506

*See footnote to Table III

TABLE V

Thermodynamic properties of $(CH_3)_3CI$ for the ideal gaseous state at one atmospheric pressure*

T° (K)	$\frac{H_0 - E_0^\circ}{T}$	= $\frac{F^\circ - E_0^\circ}{T}$	S°	C_p°
100	8.740	50.447	59.187	10.948
200	11.259	57.266	68.526	16.274
273.16	13.112	61.053	74.165	20.038
300	13 796	62.306	76.102	21.461
400	16.342	66.618	82.960	26.468
500	18.824	70.559	89.383	30.779
600	21.151	74.208	95.369	34.338
700	23.216	77.583	100.798	37.245
800	25.133	80.814	105.945	39.709
900	26.469	83.724	110.199	41.782
1000	28.440	86.757	115.200	43.565

*See Footnote to Table III

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MICROWAVE SPECTRUM OF H_2CO^{18}*

By

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Microwave spectra of formaldehyde and its isotopic species were studied by Lawrance and Strandberg[1], Okaya[2], Hirakawa et al.[3,4] and Erlandsson [5]. Hirakawa et al[4] reported only one line corresponding to the transition $1_{1,1} - 1_{1,0}$ for the molecule H_2CO^{18}. In the present investigation a sample containing 30% H_2CO^{18} has been prepared and several rotational transitions of this molecule have been observed and assigned. H_2CO^{18} was prepared by hydrolysing methylal with 30%-0^{18} H_2O^{18} in the presence of traces of concentrated H_2SO_4. H_2CO^{18} was seperated from methylal, methanol and water by pumping it through a trap at add—72°C into a liquid nitrogen cooled trap. Spectrum of $H_2C^{13}O$ was obtained using normal formaldehyde which contains 1% of C^{13} species. The observed spectra of both these molecules together with the assignment are given in Table 1. The rotational constants given in Table II have been calculated from the observed frequencies, after correcting for the centrifugal distortion, assuming the same centrifugal distortion, as given by Lawrance and Strandburg for H_2CO^{16}. Making use of the experimental data reported by Hirakawa et al. and Lawrance and Strandberg, the rotational constants for the molecules D_2CO and $H_2C^{13}O$ also have been calculated. These results are also given in Tables I and II. The structural parameters were calculated, using Karitchman's[6] equations, from these rotational constants. These are C–H distance 1.1238 ± .005 A° C–O distance 1.2119 ± .005 A° and H–C–H angle 119° 20′ ± 30′ and are very close to those given by Lawrance and Strandberg. The centre of mass condition serves as a check

$$\sum_{\alpha}^{m} \alpha \, x_{a\alpha} = 0.0092016$$

---

*The experimental work was done in the Department of Chemistry, Rice University, Houston, Texas, U. S. A.

TABLE I

OBSERVED FREQUENCIES OF H_2CO^{18} AND $H_2C^{13}O$ AND COMPARISON OF OBSERVED AND CALCULATED TRANSITION FREQUENCIES OF H_2CO^{18}, D_2CO^{16} AND $H_2C^{13}O$ IN MC/SEC.

Assignment	Obs.	Calc	Centrifugal distortion correction.
H_2CO^{18}			
$1_{1,1} \rightarrow 1_{1,0}$	4388.85*	4388.85	
$2_{1,2} \rightarrow 2_{1,1}$	13166.00	13166.03	-0.37
$3_{1,3} \rightarrow 3_{1,2}$	26330.00	26329.82	-2.49
$8_{2,7} \rightarrow 8_{2,6}$	12107.03	12107.15	-25.38
$9_{2,8} \rightarrow 9_{2,7}$	18905.80	18904.52	-44.73
$10_{2,9} \rightarrow 10_{2,8}$	28120.15	28119.71	-72.0
D_2CO*			
$1_{1,1} \rightarrow 1_{1,0}$	6096.10	6096.10	
$2_{1,2} \rightarrow 2_{1,1}$	18287.90	18287.93	-0.37
$4_{2,3} \rightarrow 4_{2,2}$	3687.28	3686.73	-2.2
$5_{2,4} \rightarrow 5_{2,3}$	8519.10	8521.23	-4.3
$6_{2,5} \rightarrow 6_{2,4}$	16759.64	16756.82	-7 8
$H_2C^{13}O$			
$1_{1,1} \rightarrow 1_{1,0}$	4593.26*	4593.26	
$2_{1,2} \rightarrow 2_{1,1}$	13778.90	13779.41	-0.37
$3_{1,3} \rightarrow 2_{1,2}$	27555,70	27556.51	-2.49
$7_{2,6} \rightarrow 7_{2,5}$	8012.56*	8012.54	-13.55
$8_{2,7} \rightarrow 8_{2,6}$	13286.8	13287.27	-25.38
$9_{2,8} \rightarrow 9_{2,7}$	20736.15	20732.96	-44.73

*Taken from reference 3 and 4.

TABLE II

ROTATIONAL CONSTANTS OF H_2CO, D_2CO ,H_2CO^{16} and $H_2C^{13}O$ in Mc/Sec.

Constant-	H_2CO*	D_2CO	H_2CO^{18}	$H_2C^{13}O$.
A	282106	141732.03	281985.57	282045.76
B	38834	32368.62	36900.50	37804.41
C	34004	26272.52	32511.70	33211.15

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POTENTIAL ENERGY CONSTANTS AND THERMODYNAMIC PROPERTIES OF SOME SELENIUM COMPOUNDS

By

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Abstract

Using the Wilson F–G matrix method, reasonable values of F–matrix elements which reproduced the observed vibrational frequencies, are determined. From these F–matrix elements, corresponding potential energy constants are calculated. The observed frequencies are used to calculate the thermodynamic properties of the molecule for 13 temperatures between 100° and 1200° K to a rigid rotor, harmonic oscillator, ideal gas approximation.

Introduction

The Raman spectra of selenium oxychloride and selenium oxyfluoride have been investigated by Gerding et al.,[1] and Rolfe and Woodward[2] respectively. In the present investigation, the potential constants of these two molecules have been evaluated using the Wilson F–G matrix method[3, 4]

Normal Coordinate Analysis

These two compounds, having a pyramidal structure, belong to the point groups C. Of the six fundamental frequencies, 4 belong to a′ type and the other two to a″ type of vibrations. All of them are active both in Raman and Infrared spectra.

The orthonormal set of symmetry co–ordinates and the elements of the kinetic energy matrix used in this investigation are the same as those obtained by Venkateswarlu et al[5, 6].

The most general quadratic potential function containing all valence forces has been used in the present investigation.

The elements of the potential energy matries are as follows:
For the a′ type:

$$\begin{bmatrix} F_{11} & F_{12} & F_{13} & F_{14} \\ & F_{22} & F_{23} & F_{24} \\ & & F_{33} & F_{34} \\ & & & F_{44} \end{bmatrix} = \begin{bmatrix} f_D & d\, f_D\beta & \sqrt{2}\, f_{Dd} & \sqrt{2}\sqrt{Dd}\, f_{D\alpha} \\ & d^2 f\beta & \sqrt{2}\, d\, f_{d\beta} & \sqrt{2}\sqrt{Dd^3}\, f_{\alpha\beta} \\ & & f_d + f_{dd} & \sqrt{Dd}\,(f_{d\alpha} \\ & & & Dd\,(f_\alpha + f_{\alpha\alpha}) \end{bmatrix}$$

For the a″ type :

$$\begin{bmatrix} F_{55} & F_{56} \\ & F_{66} \end{bmatrix} = \begin{bmatrix} (f_d - f_{dd}) & \sqrt{Dd}\, f_\alpha \\ & Dd\,(f_\alpha - f_{\alpha\alpha}) \end{bmatrix}$$

Since $F_{ij} = F_{ji}$, only the elements above the diagonal are given. In the above matrices, f_D and f_d are the Se–O and Se–X stretching force constants, f_α and f_B the X–Se–O and X–Se–X angle bending force constants respectively, and the others are the interaction constants having the usual meaning. Here X stands for either Cl or F atom.

The secular equations have been formed in the usual way and are solved to get the potential energy constants.

Results

Since there is no data available for the structural parameters of these molecules either from electron diffraction or microwave studies, the interatomic distances of similar compounds [7, 8, 9] have been made use of and are listed in Table 1. The angles are assumed to be tetrahedral.

The potential constants obtained are given in Table II. As is to be expected, the Se–O stretching force constant is almost the same for $SeOF_2$ and $SeOCl_2$. The comparatively high values of $f\beta$ and f_{dd} in the case of $SeOF_2$ may be due to the high electronegativity of fluorine, as a result which there may be an attractive force between the oxygen and fluorine atoms. A comparison of the observed frequencies and the frequencies obtained by using the potential energy constants reported here, is made in Table III.

TABLE I.

Molecular parameters of $SeOF_2$ and $SeOCl_1$

Molecules	D (A°)	d (A°)
[7, 8] $SeOF_2$	1.61	1.67
[7, 9] $SeOCl_2$	1.61	2.13

TABLE II

Potential energy constants of $SeOF_2$ and $SeOCl_2$ in 10^5 dynes/cm

Potential constants	$SeOF_2$	$SeOCl_2$
f_d	4.428	2.100
f_D	6.557	6.528
f_{Dd}	0.177	0.071
f_{dd}	1.413	0.900
f_α	0.311	0.321
$f\beta$	0.760	0.265
f_D α	0.172	0.115
f_d α	0.076	0.095
f_{dB}	0.085	0.066

TABLE III

Species.	$SeOF_2$		$SeOCl_2$	
	Observed	Calculated.	Observed	Calculated.
a'	278	278	161	161
	373	373	279	280
	664	664	388	392
	1012	1014	955	951
a''	308	308	255	256
	605	606	347	350

*From Lawrance and Strandberg, Refernce 1.

THERMODYNAMIC PROPERTIES

The heat content, free energy, entropy and heat capacity are calculated for 13 different temperatures from 100° to 1200°K making use of the observed fundamental frequencies of the above two molecules given in Table III. A rigid rotor, harmonic osillator approximation is assumed and the values are calculated for the ideal gaseous state at 1 atmospheric pressure. The nuclear spins and isotopic mixing are neglected. The moments of inertia were calculated using the structural parameters given in Table I. The symmetry number is 1. The thermodynamic properties for $SeOF_2$ and $SeOCl_2$, thus obtained are listed in Tables IV and V.

TABLE IV

THERMODYNAMIC PROPERTIES OF $SeOF_2$ FOR THE IDEAL GASEOUS STATE AT ONE ATMOSPHERIC PRESSURE.*

T°(K)	$(H_0 - E_0°)/T$	$-(F° - E_0°)/T$	S°	Cp°
100	8.255	50.151	58.392	9.333
200	9.701	56.274	65 979	12,811
273.16	10.795	59,469	70.264	14.636
300	11.171	60.501	71.672	15.177
400	12.357	63.872	76.229	16.632
600	13.314	66.734	80.048	17.560
600	14 074	69.234	83.308	18.152
700	14.692	71.460	86.150	18.554
800	15.194	73.462	88.656	18.833
900	15.606	75.272	90.878	19.032
1000	15.953	76.921	90.875	19.180
1100	16.260	78.483	94.743	19.296
1200	16.507	79.877	96.385	19.342

*H_0 = heat content; $F°$ = free energy; $S°_0$ = entropy; $Cp°$ = heat capacity at constant pressure; T = temperature in degrees Kelvin; $E_0°$ = energy per gram-molecule of tne perfect gas at T = 0°K and all the quantities are in cal. deg^{-1}. $mole^{-1}$.

TABLE V

THERMODYNAMIC PROPERTIES OF $SeOCl_2$ FOR THE IDEAL GASEOUS STATE ONE ATMOSPHERIC PRESSURE.*

T° (K)	$(H_0 - E_0°)/T$	$-(F° - E_0°)/T$	S°	Cp°
100	8.895	52.978	61.873	11.132
200	11.134	59.851	70.985	15.058
273.16	12.392	63.518	75.910	16.472
300	12.775	64.703	77.478	16.836
400	13.919	68.535	82.452	17.811
500	14.765	71.755	86.520	18.402
600	15.401	74.477	89.878	18.783
700	15.913	76.930	92.843	19.040
800	16.308	79.054	95.362	19.173
900	16 633	80.967	97.600	19.339
1000	16.913	82.761	99.674	19.436
1100	17.150	84.412	101.562	19-507
1200	17.357	85.958	103.315	19.564

*See footnote to Table IV.

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ON THE GROWTH OF PEA, GERANIUM AND TOMATO UNDER THE INFLUENCE OF MUSICAL SOUNDS

By

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(Communicated by Professor T. C. N. Singh, Annamalai University.)

INTRODUCTION

On reading through an article entitled, "*Grow your plants to music*" published in the *Science Digest* (10), I was spurred to get interested in this kind of experiment with a view to carry through a research-project for presentation to the Science Fair at Alexandria (Louisiana, U. S. A.). Subsequently, I got in touch with Professer T. C. N. Singh of the Annamala, University who furnished me with interesting and valuable literature and also guidance in the line. I owe a deep debt of gratitude to the professor for this.

Although quite a good deal of work has been done in this direction with a number of ornamental and economic crop-plants (1-9 & 11-13. but nothing so far has been done with Pea, Geranium and Tomato) Therefore, these plants were selected and experimented upon. The resultst obtained have been found interesting and as such they have been presented herein briefly for stimulating active interest amongst the biologists. Actual specimens were exhibited in April, 1962 at Alexandria (Louisiana, U. S A.) in the Science Fair (Plate Photograph-1.)

PROCEDURE

The method of testing used is a standard procedure designed to establish comparative results in research. Several groups of plants were planted at different times. Each groups consisted of four pots, each containing from one six or seven plants, depending on the kind of plant. One plant out of each group was set aside as the control plant. It was grown as usual, and was kept in almost complete silence. The other three plants were the experiment plants. They were treated the same as the control plant except that they were exposed to thirty minutes of music each

morning. The experimental plants in each group, were grown by treatment with different type of music. The three types of music used were *classical rock and roll*, and *religious*. The following records were used:

(a) *Classical Music:* "The Frank Liszt story" performed by Carmen Cavallaro at the Piano and Orchestra directed by Jack Pleis; and "Roger Willams Greatest" Hits performed by Roger Williams at the Piano and back-ground orchestra.

(b) *Rock and Roll Music:* "Something for Everybody" performed by Elvis Presley; and "Your Twist Party" perfomed by Chubby Checker.

(c) *Religious Music:* "Someone watching over you" performed by Jimmie Davis with Plainsmen; and "No one stands alone" performed by Don Gibson.

Otherwise the control and experiment plants were treated in the same manner viz. all the plants were planted at the same time in the same type of soil. The water for each plant was carefully measured, and all the plants of each group were watered at the same time. All the plants were exposed to equal quantum of day light. They were all kept in same spot insuring that they were grown under similar temperature.

Each morning the experiment plants were exposed to thirty minutes of music. They were taken to another spot and the type of music they were grown by was played. Then that group was returned to the original spot. This continued untill each experiment plant had been exposed to its type of music. The experiments began at approximately at six thirty each morning. They were begun on December 16, 1961, and were completed on April 14, 1962. Except for the four or five days that the project was being displayed in Science Fair, the experiments were done everyday.

RESULTS

All of the testing of the plants, proved that music does have a definite effect on plant growth. The sound-treated plants grew better, were healthier, matured earlier, and had greater yields. The amount of increase in growth depended on the type of music with which they were treated.

English peas : The rock and roll music was the best stimulator (Plate Photograph-2). In all experiments, this plant was the tallest. It was the first to bloom and make a pea. This plant also had many more blooms than the other peas. The classical music was the second best stimulant. It was approximately one week behind the rock and roll in blooming. The third best stimulant was the religious music. The control plant was never as tall as any of the others. In two groups this plant died due to cold weather which shows that it was not as healthy as the others as they did withstand the severe weather conditions.

Geraniums : The results in height were the same as in the English peas namely that the experimental plants had grown appreciably taller than the control plants (See Graph-I and Plate Photograph-3 & Table-I). Results in height were the only results obtained from experiments with these, as they had not bloomed when this paper was written.

Tomatoes : The results with this group are slightly different from the rest. The classical music was the best stimulant in all cases with the tomatoes. The rock and roll second and religious third. Height differences were the only significant results in these tests also (See Graph-II and Plate Photograph 4 and Table-II).

CONCLUSIONS

Music does stimulate stem growth. Music treated plants are taller than those grown without music. Different types of music Produce different degrees of stimulation. The faster the beat of the music, the more the growth of the plant is speeded up. These experiments tend to show that music produces earlier maturity and greater yields.

SUMMARY

Mrs. Swedlow's article entitled "Grow your plants to music" published in *Science Digest* 1961, spurred the author to undertake experiments on similar lines on English Pea, Geranium and Tomato by irradiating them with (a) *Classical Music*, (b) *Rock and Roll Music* and (c) *Religious Music.*

The experiments were performed with proper and strict controls in each case. The results achieved were astounding:

English Peas : The *Rock and Roll Music* was the best stimulator, the second best being the *Classical Music* and the third the *Religious Music.*

The control plants were never as tall as any of the above three. All the experimental plants were the first to bloom and to make pea-pods.

Geronium: The results in height were exactly the same as in the English Peas, namely all the experimental plants in order had grown appreciably taller than the control plants.

Tomatoes: In this case the *Classical Music* proved to be the best of all, *Rock and Roll* and *Religious Music* occupying the second and third places respectively. The control plants were definitely subordinate in performance to the experimental plants.

In conclusion it may be remarked based on these observations that musical sounds do stimulate the growth of plants. Musical sound treated plants are undoubtedly taller than those grown without it and had flowered and fruited earlier than their control counterparts.

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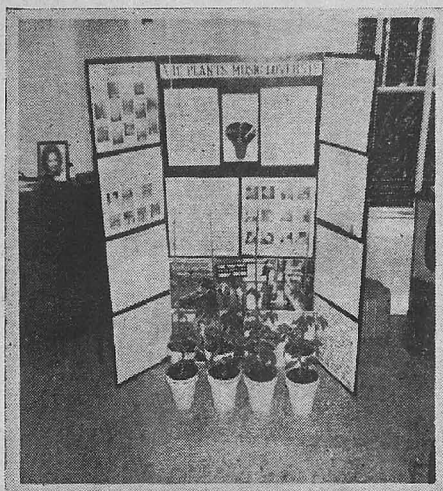
EXPLANATION OF PLATE

PHOTOGRAPH–1 : Showing the set-up exhibited at the Science Fair at Alexandria, Louisiana, U. S. A. in April 1962.

PHOTOGRAPH–2 : Showing the growth of English Pea, The treatment of Rock and Roll has produced comparatively taller growth in the experimental plants on the right.

PHOTOGRAPH–3 : Showing similar enhanced growth in Geranium plant treated with Rock and Roll.

PHOTOGRAPH–4 : Showing that best enhanced growth was noticed in Tomato treated with classical music.



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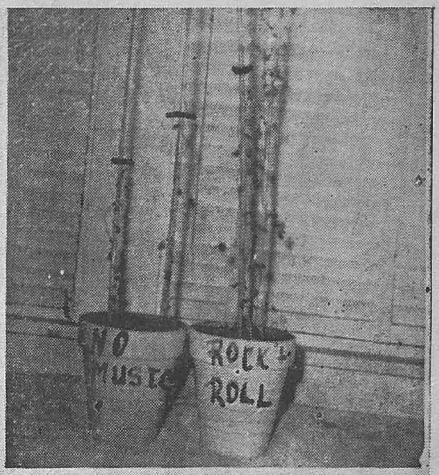

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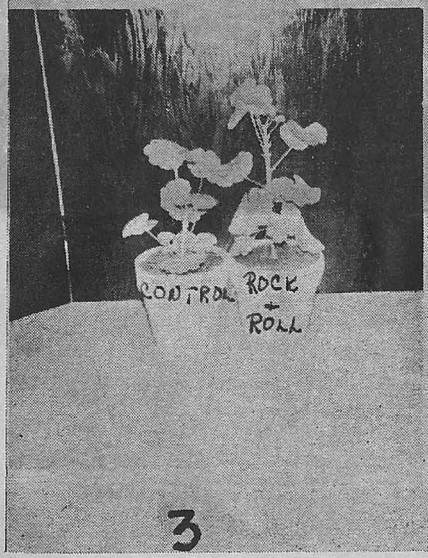

3

4

For Graph I and II – See page facing 49.

TABLE — I TOMATO

(Growth in length of shoot in inches)

Date	Control	Classical	Religious	Rock and Roll
19th March	3.0	3.0	3.0	3.0
20th ,,	3.4	3.8	4.2	4.8
21st ,,	3.5	3.9	4.6	5.5
22nd ,,	3.7	4.4	4.8	5.9
23rd ,,	4.0	5.0	5.0	7.0
24th ,.	4.6	5.5	5.8	7.5
25th ,,	5.2	6.0	6.5	8.3
26th ,,	6.0	7.0	7.4	9.0
27th ,,	6.4	7.6	8.3	9.4
28th ,,	6.6	8.0	8.5	9.7
29th ,,	6.8	9.0	8.7	9.9
30th ,,	7.0	9.4	9.0	9.9
31st ,,	7.3	9.8	9.4	10.2
1st April	7.6	9.9	9.5	10.4
2nd ,,	7.7	10.0	9.6	10.6
3rd ,,	7.8	10.5	10.0	10.7
4th ,,	8.0	11.0	10.4	11.0
5th ,,	8.2	11.4	10.6	11.0
6th ,,	8.4	13.0	11.0	11.5
7th ,,	8.6	13.8	11.4	12.0
8th ,,	8.7	15.4	11.7	13.0
9th ,,	8.8	16.5	11.8	13.5
10th ,,	9.0	17.2	11.9	13.8
11th ,,	9.5	18.0	12.0	14.0
12th ,,	9.6	—	13.0	14.5

TABLE — II (GERANIUM)

(Growth in length of shoot in inches)

Date	Control	Classical	Religious	Rock and Roll
19th March	5.0	6.0	6.6	7.0
20th ,,	5.4	6.4	7.0	7.5
21st ,,	5.5	6.7	7.2	7.6
22nd ,,	5.6	7.0	7.4	7.7
23rd ,,	6.0	7.2	7.6	7.7
24th ,,	6.2	7.4	8.2	8.6
25th ,,	6.3	7.6	8.5	8.8
26th ,,	6.5	7.7	8.6	8.9
27th ,,	6.7	8.0	8.8	9.0
28th ,,	6.8	8.3	8.9	9.4
29th ,,	7.0	8.5	9.0	9.6
30th ,,	7.2	8.7	9.0	9.8
31st ,,	7.6	8.8	9.4	9.9
1st April	7.7	8.9	9.5	10.0
2nd ,,	8.0	9.0	9.7	11.0
3rd ,,	8.3	9.0	10.0	11.6
4th ,,	8.6	9.2	10.2	11.7
5th ,,	9.0	9.3	10.3	11.9
6th ,,	9.2	9.5	10.4	12.5
7th ,,	9.4	9.7	10.6	12.7
8th ,,	9.5	9.8	10.6	12.8
9th ,,	9.6	9.8	10.7	13.0
10th ,,	9.7	10.0	10.8	13.5
11th ,,	9.8	10.5	10.8	13.9
12th ,,	10.3	10.7	10.9	14.0

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