FORMATION OF RESONANT STATES IN $K^-n \rightarrow \pi^0 \Sigma^-$ BETWEEN 1850 AND 2160 MEV

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Results are presented for a partial-wave analysis of the $l=1$ reaction $K^-n \rightarrow \pi^0 \Sigma^-$ covering a range of CMS energies from 1850 to 2160 MeV. The events used were obtained from the interactions of the type $Kd \rightarrow \pi^0 \Sigma^- p_s$. Values of the resonance parameters of the $Y^*_1 (2030)$ were determined. In addition, it was found that $F_{\pi^0}$ amplitude resonates at ~ 1980 MeV whose parameters differ significantly from $Y^*_1 (1910)$ but in better agreement with the new $Y^*_1 (1940)$ reported by Barnes et al.5

1. Introduction

Several $Y^*_1$ resonances have been reported to exist in the energy region 1800-2200 MeV. Of these, the $Y^*_1 (2030)$ with spin parity $J^P=7/2^+$ is well established. Positive evidence for a $Y^*_1 (1910)$ with $J^P=5/2^+$ has been found in total cross-section data 2,3 and in an analysis of several formation experiments.4 In addition, a recent production experiment3 suggests a resonance, $Y^*_1 (1940)$ with parameters different from those of the $Y^*_1 (1910)$. In particular there is a strong disagreement between the ratios of the $\pi^0$ and $\pi^\pm$ branching fractions for the two resonances.

In this paper we present results of an energy-dependent partial wave analysis of the pure $l=1$ reaction $K^-n \rightarrow \pi^0 \Sigma^-$ covering the CMS energy region from 1850 to 2160 MeV.

2. Experimental Details

The experiment was performed at the Rutherford High Energy Laboratory by exposing the 80-cm Saclay bubble chamber filled with liquid deuterium to a two-stage electrostatically separated $K^-n$ beam. Two exposures were made, at beam momenta of 1.45 and 1.65 GeV/c and yielding, respectively, 3.0 and 1.6 events per microbarn from a total of approximately 700,000 pictures.

The motion of nucleons inside the deuteron enabled us to study $K^-n$ interactions over a range of CMS energy from 1850 to 2160 MeV. The beam had a momentum resolution of \( \pm 1\% \) found by kinematically fitting the decays occurring inside the chamber.

The events under study include only those with one or two prongs with kink on one track. Long and curved kink tracks were rejected at the scanning stage in order to include only the strange particle decays. Events with an odd number of prongs or with a visible slow proton were selected as possible $K^-n$ interactions and were measured on SMPS or conventional machines. They were then analysed using either the RHEL or CERN geometrical reconstruction and kinematical fitting programmes.

Events with invisible spectator protons were constrained in the kinematical fit to satisfy the following relationship between the 3 momentum components:

\[
P_x = P_y = P_z = (0.0 \pm 30) \text{ MeV/c}
\]

the error allowing for the Hulthen distribution; the increased error in $P_z$ takes into account the decreased detection efficiency for short proton tracks along the optical axis. The momentum distribution for inserted spectators joined smoothly onto that for seen spectators and agreed approximately with that predicted using a Hulthen wave function for the deuteron.

3. Selection of $K^-n \rightarrow \pi^0 \Sigma^-$ Events

Since there is a missing $\pi^0$ involved in this reaction, therefore, the fits with unseen spectators should not be considered reliable for the partial wave analysis. In view of this events only with a seen spectator proton were retained for analysis. A total of 1589 events fitted this reaction channel out of which 545 with seen spectators < 280 MeV/c. The following selection criteria were adopted to pick the best possible sample of events:

(i) **Missing Mass Selection.**—The reaction

\[
K^-d \rightarrow \Sigma^- p \pi^0
\]

could be ambiguous with

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ANOMALOUS BEHAVIOUR OF SOLUTIONS OF SIMPLE AROMATIC COMPOUNDS IN STRAIGHT CHAIN HYDROCARBONS AND MINERAL OILS

Part III.—Further Viscosity Measurements in Some Binary Systems, and Development of a Formula for Predicting the Free Energy of Mixing for Aromatic Compounds

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The previously reported measurements of viscosity depression and free energy of mixing have been repeated in case of benzene and toluene, now mixed with nonane and octane, respectively, in place of octane and heptane previously used. The previous results are generally confirmed, and mean values of 171±20 and 102±15 cal/mole for $\Delta G_m$ are obtained for benzene and toluene, respectively.

The data for nine aromatic compounds so far studied are analyzed, and a least-squares treatment gives the following relation as a first approximation:

$$\Delta G_m = 180+70\times (\text{No. of phenolic groups})$$

This fits the observed values of $\Delta G_m$ to within±18 cal/mole r.m.s., except in case of phenol, for which the observed value of $\Delta G_m$ is 295, i.e. 45 cal/mole higher than that predicted by the formula. Further studies on xylencs and similar compounds are in hand for elucidation of the remaining second-order effects.

1. Introduction

For ideal behaviour of the viscosity of mixtures of two constituents A and B in molar proportions $X_A$ and $X_B$, two theoretical relations have been proposed, viz.

$$\ln \eta_{\text{ideal}} = X_A \ln \eta_A + X_B \ln \eta_B$$

and

$$\eta_{\text{ideal}} = X_A \eta_A + X_B \eta_B$$

where $\phi = 1/\eta$ is the fluidity, i.e. the reciprocal of dynamic viscosity. It is readily shown that these two relations can be approximated to by

$$\ln \eta_{\text{ideal}} = X_A \ln \eta_A + X_B \ln \eta_B$$

and

$$\eta_{\text{ideal}} = X_A \eta_A + X_B \eta_B$$

provided $\eta_A$ and $\eta_B$ are not appreciably different, and this is approximately equivalent to

$$\eta_{\text{ideal}} = X_{AV_A} + X_{BV_B}$$

since the changes in density are generally much smaller than those in $\eta$. (Also, $X_A$ and $X_B$ can often be replaced by proportions by weight or volume of the components A and B, provided that molecular weights and densities of the two liquids are not very much different.) Departures from these linear relationships are measured as the viscosity depression $\Delta \eta$ or $\Delta \eta$.

In the previous communications relating to viscosity measurements of long-chain phenolic compounds mixed with appropriate mineral oils, it was shown that the fractional viscosity depression ($\Delta \eta/\eta_{\text{ideal}}$) is correlated as much with the actual viscosity of the mixture, as well as that of the number of active hydroxylic groups. This prompted the investigation of similar compounds without a long side-chain, such as allylphenol and allyltoluene, and cyclohexane and benzene, when mixed with suitable straight-chain hydrocarbons or mineral oils, in Part I of this series. In Part II, viscosity measurements were undertaken on toluene-heptane and phenol-mineral-oil systems from 5°C to 40°C and 60°C to 120°C respectively, and fractional viscosity depressions of the order of 6% and 20% respectively, were found in these two systems at 40°C. This corresponds to free energy of mixing, $\Delta G_m$, of the magnitude of 89 and 295 cal/mole, respectively, using the semiempirical formula

$$\Delta G_m = 2.45 \times RT \ln \left( \frac{\eta_{\text{ideal}}/\eta_{\text{exp}}}{\eta_{\text{ideal}}} \right) \approx 2.45 \times RT \left( \frac{\Delta \eta/\eta}{} \right)$$

In Part I of this series, the measurements on the benzene-heptane system from 15°C to 40°C at intervals of 5°C yielded the free energy of mixing as about 180 cal/mole, and the plot of maximum relative viscosity depression ($\Delta \eta/\eta_{\text{ideal}}$) showed an anomalous variation with temperature in the region of 30°C to 35°C. The experiments could not be taken to higher temperatures because of preferential loss of heptane. The large viscosity depression ($\Delta \eta/\eta_{\text{ideal}}$) of the order of 10% to 20% can be understood as being due to polar interaction of the benzene nucleus through residual intermolecular forces (emanating from the resonating electrons of its ring), and the temperature variation anomaly, though unexpected, is in consonance with the measurements on the flow activation
INVESTIGATION OF THE CHARACTER OF THE JUMPS IN ACTIVATION ENERGY OF VISCOSITY FLOW IN PURE LIQUIDS AND SOLUTIONS. PART IV

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Further study of the bulk and the boundary-induced effect in the activation energy jumps observed in pure liquids and aqueous solutions was undertaken by determining the flow activation energy of dilute aqueous solutions of ethylene glycol, using three viscometers of different capillary bore. It has been confirmed that the whole phenomena of discontinuity observed in pure liquids and aqueous solutions are more or less equally dependent on the two basic causes viz. bulk aggregation and boundary-layer, and the latter does not extend much beyond 0.4 mm i.e. 400μ. The results show that almost half of the observed jumps, i.e. those at 15°C, 22°C, 27°C and 42°C, are not affected substantially by changing the diameter or by addition of glycol up to 15%, and can be presumed to be definite bulk phenomena.

1. Introduction

Detailed studies on the influence of temperature and of concentration of foreign molecules on the activation energy jumps observed in pure water were undertaken in these laboratories, with a number of aqueous systems, such as water-ethanol,1,2 water-sodium chloride3,4 and water-ethylene glycol.5 In the course of these studies, it has been tentatively observed that the jumps or discontinuity found in the structural properties of water are functions of the temperature and the concentration of the foreign molecules. The movements of these jumps with concentration are found to be more or less uniform in character, but in certain regions there is appearance, disappearance and even coalescence of some of the steps, with a change in magnitude of the jumps. The manifestation of such characteristic features in the structural properties of liquid water clearly shows that the observed phenomena may be the result of more than one isolated cause or a combination of them. It is, therefore, necessary to make a full investigation of the character and the origins of these jumps.

Some preliminary investigation has already been done by Qurashi and his coworkers6,7 by making a synoptic analysis of the refractometric measurements on water–ethanol systems taken with grazing and nongrazing incidence, and also by viscometric measurements taken with viscometers of different capillary diameters. It was found that in the range from 20°C to 50°C only the activation energy jumps at 22°, 27°, 42° and 48°C could be definitely considered as authentic anomalies in the bulk properties of water, while the rest are induced or augmented by the glass–liquid interfacial boundary. Further experimental investigation has, therefore, been carried out by extending the measurements on flow activation energy of pure water, as well as by carrying out these measurements with another aqueous system, namely water–ethylene glycol, using three viscometers of different capillary diameters.

2. Measurements with Pure Water

Accurate activation energy data on pure water at one degree intervals in the range from 20° to 50°C, using two viscometers of capillary bore 0.50 mm and 0.71 mm, have already been reported and discussed in the earlier communication.6 Graphical comparison of the two separate sets of data brought out the fact that the additional jumps at 34°C and 37°C appearing in the data obtained with the finer viscometer of capillary bore of 0.50 mm are largely smoothed out with the use of the wider bore. This significant development is now followed up by (a) extending down to 10°C the measurements previously carried out with the viscometer of capillary bore of 0.71 mm, and (b) making further redeterminations of $E_\text{f}$ for pure water in the range of 10°-45°C, using a still wider viscometer of capillary bore 0.88 mm. The redetermination of $E_\text{f}$ could not be made over the whole range from 10° to 50°C, because of the significant increase of experimental error in the measurement of times of flow, and the consequent individual error in $(E_\text{f}/R) \pm 1000$, due to very small flow times above 40°C.
THE E_{010} CAVITY RESONATOR, THE TEMPERATURE VARIATION OF RESONANT FREQUENCY, THE RESONANCE CURVES AND THEIR ANALYSIS

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An E_{010} circular cylindrical cavity resonator has been designed and constructed to investigate the dielectric properties of different dielectrics. Described in the paper are the temperature variation of resonant frequencies and the experimental techniques to draw the Q-curves of the air-filled and loaded cavity resonator at 10 cm wavelength band.

The shapes of the resonance curves have been analysed graphically with the help of the equation written by analogy with the equation derived to analyse the shape of the square-law response curve of the H_{01} resonator. The form in which it may be fitted to the observed Q-curves is

\[ \frac{1}{ID'2} = \frac{1}{D_0} \left( 1 + \frac{1}{2} \left( \frac{f_0}{f_0 + f} \right)^2 \right) \]

where \( f_0 \) and \( D_0 \) are respectively the resonant frequency and the resonance power output. The equation is

where \( \lambda_0 \) and \( \lambda_0 \) are respectively the resonant frequency and the fundamental frequency of the H_{01} resonator.

The E_{010} Cavity Resonator

The E_{010} cavity resonator of radius \( a = \lambda_0 / 2.6125 \) = 3.76 cm and length, \( l = 6 \text{ cm} \) (where \( \lambda_0 \) is the resonant wavelength of the air-filled cavity) is bored out of a solid brass cylinder with slightly larger radius than required and given a thick silver coating and then machined to obtain the required radius. The ends are fitted with two flat removable lids which are also coated with silver and secured by a set of screws. Care is taken during turning, reaming and lapping of the inner surface of the cavity so as to obtain a constant diameter over the whole length (within \( \pm 0.02 \text{ cm} \)). Surfaces of the cavity and lids are kept clean and polished to obtain high quality factor. The E_{010} resonator is shown in Fig. 1.

Two 1-cm diameter holes are provided at diametrically opposite points on the curved surface of the cavity midway between the ends, to hold the input and output magnetic loop-probes. The semi-circular loops, projected nearly 3 mm inside the cavity are made out of the inner conductor of Pyrotenax coaxial cable. The planes of the loops are kept parallel to the axis of the cavity in order to link with the magnetic field. The loop-probes are fitted with screws and lock assembly so that the depth of penetration of the loops inside the resonator can be changed without altering the position of their planes to obtain best feed in and pick-up of power.

The specimen is held central along the axis of the cavity with the help of a 3.5-cm long brass plug with adjustable hole fitted on top lid and a hole drilled at the centre of the bottom lid (The specimen is central to within 0.1 mm at the two ends). The E_{010} mode is the lowest frequency mode of the circular cylindrical cavity and is characterized (for perfectly conducting boundaries) by a purely longitudinal electric field and a purely circumferential magnetic field. The field distribution is shown in Fig. 2. In practical resonator the finite conductivity of the wall material and the presence of the probes produce deviations from the ideal field distribution but the overall...
FORMAL REDOX POTENTIAL VALUES OF CO\textsuperscript{3+}/CO\textsuperscript{2+} SYSTEM REGARDING THE USE OF COBALT(III) ACETATE AS VOLUMETRIC OXIDIMETRIC TITRANT

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The values of formal redox potential of Co\textsuperscript{3+}/Co\textsuperscript{2+} system have been measured in hydrochloric, perchloric, acetic and sulphuric acids. The change in the values with changing concentrations of these acids have also been investigated.

Recently, investigations on the use of cobalt(III) acetate as volumetric titrant have been made for the quantitative oxidation of organic and inorganic systems.\textsuperscript{1} Cobalt(III) acetate exhibits very strong oxidising properties and its redox potential, the main cause of its vigor, has been measured to be 1.84 V in 4N HNO\textsubscript{3}.\textsuperscript{2} The titrant has yielded very useful results and a lot still remains to be investigated. Hanif\textsuperscript{3} has successfully tried various quantitative determinations of organic and inorganic substances in various acidic media. It was, therefore, advisable to study the value of redox potentials which could positively confirm and give information about the possible utility of the titrant and the medium before actually trying the Co\textsuperscript{3+}/Co\textsuperscript{2+} system. These studies have been conducted in those media which could be safely used for such further important studies and the results of these findings have been reported in this communication.

**Experimental**

*Reagents.*—Cobalt(III) acetate solution in glacial acetic acid was electrolytically prepared according to the method of Sharp and White\textsuperscript{3} modified by Hanif.\textsuperscript{1} The factor of this solution was determined with ferrous sulphate using potentiometric end point method.

Cobalt(III) acetate solutions of other strengths were also prepared in glacial acetic acid by diluting stock solution and checking their strengths as above. All other chemicals used were also of analytical grade.

*Apparatus.*—Potential measurements were made with an electronic pH meter with platinum indicating and saturated calomel reference electrodes. After each reading both electrodes were washed with distilled water and the platinum electrode was rubbed between the folds of filter paper to remove any possible adherence of the reactants to its surface. All the potential values were converted for standard hydrogen electrode.

Method of Measurement of Formal Redox Potential.—Formal redox potential values were measured either through the courses of potentiometric titration curves of suitable systems, measuring the potential value at double the reagent consumption required for equivalence, or measuring these values of an equimolar mixture of oxidised and reduced forms of the system Co\textsuperscript{3+}/Co\textsuperscript{2+}. These studies were conducted at a temperature of 25°C. All the values of formal redox potential reported in this work are the average of multiple measurements.

**Results**

**Formal Redox Potential of Co\textsuperscript{3+}/Co\textsuperscript{2+} in Hydrochloric Acid Medium.**—The first method of potential measurement was used. Advantage was taken of the fact that divalent iron in 2N HCl reacts quantitatively with trivalent cobalt. For 1, 3 and 4N HCl no suitable system was available, hence the second method of measurement was used. The results of the findings have been reported in Table I.

**Formal Redox Potential of Co\textsuperscript{3+}/Co\textsuperscript{2+} in Perchloric Acid Medium.**—According to the previous studies,\textsuperscript{1} perchloric acid from 1 to 10% was found to be well suited to redox measurements with cobalt(III) acetate as oxidizing titrant. It was, therefore, rational to measure formal redox potential values of Co\textsuperscript{3+}/Co\textsuperscript{2+} system in perchloric acid medium as this could give very important advance information regarding the suitability of this medium for redox studies of any substance with cobalt(III) acetate. These experiments were conducted only according to the second method of measurement as no suitable system was available regarding the application of the first one. The results of the investigations are given in Table I.

**Formal Redox Potential of Co\textsuperscript{3+}/Co\textsuperscript{2+} in Acetic Acid Medium.**—The values of formal redox potential of Co\textsuperscript{3+}/Co\textsuperscript{2+} system were measured in acetic acid ranging from 50 to 99%. Results of these measurements have been exhibited in Table I.

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We have recently reported the isolation of complexes from dihydrazides with nickel(II) and cobalt(II) salts.\(^2\) In each case the compounds had two molecules of water coordinated to the metal. We have therefore attempted the preparation of such aquo-complexes with simple ligands. The hexaacetamido complex of nickel has already been reported.\(^3\) We had noted the formation of some of the acetamide complexes from the study of such physical properties as the density and the viscosity of a univariant system of nickel chloride and acetamide and found the formation of complexes in the 1:4 and 1:6 proportion.\(^4\) With these results in mind we report here the preparation and properties of the diaquatetraacetamido complexes of nickel(II).

Experimental

The hydrated nickel chloride and bromide were partly dried at 110°C so as to obtain the dihydrates. Nickel iodide was prepared by refluxing the chloride and acetamide in the I\(_2\)Cl\(_2\) proportion.\(^4\) Nickel nitrate in stoichiometric proportion. Nickel iodide was prepared by refluxing the nitrate in butanol. The partly dehydrated nickel salt and acetamide in the I\(_2\)Cl\(_2\) were partly dehydrated by refluxing its hexahydrate in butanol or methanol for 1 hr. The solution so obtained was concentrated by distilling off some of the alcohol. The tetracetamido compound was further purified by washing with chloroform to remove the traces of acetamide. The compounds were desiccated over sulphuric acid. No loss in weight was observed even when kept for several days.

It was not possible to crystallize these complexes from any solvent since in each case a displacement of the amide was observed. In the case of ammonia, aniline, pyridine and bipyridine the corresponding complexes were obtained which were identified spectroscopically but with acetonitrile, acetone, nitromethane and boiling chloroform acetamide was displaced giving anhydrous nickel salts. An aqueous solution gave free acetamide and the hydrated nickel salt. This was confirmed by the NMR spectrum recorded in D\(_2\)O which gave a broad band for the amide in the 100 c/s region. (Found: C, 23.65; H, 6.03; N, 13.6; Ni, 14.1; Cl, 17.49%; m.p. 115°C. Calc. for [Ni(Acam\(_4\)](H\(_2\)O)\(_2\)Cl\(_2\): C, 23.91; H, 6.02; N, 13.94; Ni, 14.61; Cl, 17.64%.) (Found: C, 19.93; H, 5.13; N, 11.45; Ni, 11.50; Br, 32.41, m.p. 132°C. Calc. for [Ni(Acam\(_4\)](H\(_2\)O)\(_2\)Br\(_2\): C, 19.61; H, 4.82; N, 11.42; Ni, 11.96; Br, 32.56%.) (Found: C, 16.6; H, 4.1; 4.1; N, 9.3; Ni, 10.3; I, 43.13; m.p. 98-100°C. Calc. for [Ni(Acam\(_4\)](H\(_2\)O)\(_2\)I\(_2\): C, 16.44; H, 4.21; N, 9.58; Ni, 10.02; I, 43.39%.) (Found: C, 21.61; H, 5.2; N, 18.7; Ni, 12.3; m.p. 102°C. Calc. for [Ni(Acam\(_4\)](H\(_2\)O)\(_2\)NO\(_3\): C, 21.12; H, 5.32; N, 18.48; Ni, 12.29%.)

IR spectra were recorded on a Perkin Elmer Model 237 spectrophotometer using KBr pellets and nujol mulls. The visible spectra were recorded on Unicam SP 500 and Beckman DK\(_2\) spectrophotometers. The spectra were run in methanolic solutions and concentrations were adjusted so as to obtain the optical density at \(\lambda_{\text{max}}\) in the range of 0.5-1.0. Magnetic susceptibility measurements were made on a Gouy magnetic balance using powdered samples. Conductivity was measured on a WTW conductivity meter type LBr, using extra pure methanol as solvent.

Results

From the analytical data it is apparent that nickel is hexa-coordinated; the conductivity measurements which appear in Fig. 1 suggest the formulation [Ni(Aacetamide)\(_4\).2H\(_2\)O]X\(_2\) for these compounds. The bands in the IR spectra are listed in Table 1 along with their assignments. Fig. 2 depicts the absorption in the visible region of the spectrum and Table 2 lists the band assign-
Alkylation agents of various types probably constitute the largest single group of antitumour agents, and of these nitrogen mustards have received most attention. This pharmacological activity has been shown in a number of substituted benzo[b]thiophenes particularly in case of 5-bromo-N-ethyl-N-(2-chloroethyl)-3-aminomethylbenzo[b]thiophene hydrochloride. However, very low solubility of the compound necessitated the preparation of some soluble salts. It was also decided to substitute chlorine by fluorine in the preparation of some soluble salts. Methane-sulphonic acid and citric acid were used for the salt formation of 1.

The compounds of the general structure which were prepared were limited to the derivatives of 5-H and 5-bromobenzo[b]thiophene. Methanesulphonic acid and citric acid were used for the salt formation of 1.

\[
\text{R} = \text{Br}, \text{H}
\]

The products were isolated as colourless plates in 80% yield.

Synthesis of the fluoro compounds proved more difficult. Condensation of 5-bromo-3-(bromomethyl) benzo[b]thiophene with an excess of anhydrous ethylamine gave N-ethyl-3-(aminomethyl) benzo[b]thiophenes in 70-80% yield. These secondary amines were then converted into the required fluorines containing t-aminos by condensation with 0.5 moles of 1-bromo-2-fluoroethane in boiling ethyl methyl ketone. Treatment of the t-amine with ethereal solution of hydrogen chloride gave the crystalline salts in 40% yields.

**Experimental**

5-Bromo-N-ethyl-N-(2-chloroethyl)-3-aminomethylbenzo[b]thiophene Methanesulphonate.—5-Bromo-N-ethyl-N-(2-hydroxyethyl)-3-aminomethylbenzo[b]thiophene and its corresponding 2-chloroethyl derivative were prepared as described in the literature. 2

To a solution of the free base (5 g) in dry ether (100 ml) was added an ethereal solution of methanesulphonic acid (1.5 g). An oil separated out, which solidified on standing. The product was filtered off, washed with water and crystallised from dry ethanol to give the corresponding salt as colourless plates. Similarly, citrate and methanesulphonate salts of 5-bromo-N-ethyl-N-(2-hydroxyethyl)-3-aminomethylbenzo[b]thiophene were prepared. Details are given in Table 1.

5-Bromo-N-ethyl-N-(2-fluoroethyl)-3-aminomethylbenzo[b]thiophene Hydrochloride.—5-Bromo-3-(bromomethyl) benzo[b]thiophene (27.4 g) and an excess of ethylamine (21.9 g) were dissolved in dry benzene (200 ml), and the mixture was boiled for 30 min. Ether (300 ml) was added to the cold reaction product and the precipitated solid was filtered off. The filtrate was washed several times with water and dried (MgSO₄). The product 5-bromo-N-ethyl-3-aminomethylbenzo[b]thiophene was obtained as an oil after distillation of the solvent under reduced pressure. The hydrochloride was prepared in the usual way and was crystallised from dry ethanol as colourless needles, m.p. 203-204°C, yield 70%. (Found: C, 43.3; H, 4.5; N, 4.2. C₁₇H₁₃NSBrCl; requires: C, 43.1; H, 4.2; N, 4.5.)

5-Bromo-N-ethyl-N-(2-fluoroethyl)-3-aminomethylbenzo[b]thiophene.—1-Bromo-2-fluoroethane (12.7 g, 0.1 mole) and 5-bromo-N-ethyl-3-aminomethylbenzo[b]thiophene (54 g, 0.20 mole) were heated under reflux in ethyl methyl ketone (100 ml) for 16 hr. The mixture was cooled, filtered and to the filtrate was added dry ether (100 ml). It was again filtered and the filtrate was dried (MgSO₄). The solvents were removed, the residue was dissolved in 6N HCl and the insoluble material extracted with methylene chloride. The residue was made alkaline with sodium hydroxide,
SHORT COMMUNICATION
PHYSICAL SCIENCES SECTION


CHEMICAL INVESTIGATION OF THE LEAVES OF CADABA FRUTICOSA

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CHEMICAL INVESTIGATION OF GERMINATED PEGANUM HARMALA SEED

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FRACTIONATION OF PECTINS

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Samples of pectin were extracted from ethanol–water–extracted orange peels and turnips (Brassica napiformis) in a stepwise manner with water, ammonium oxalate and ethylenediaminetetraacetate (EDTA) solutions. Pectin samples were examined for (a) uronic acid anhydride contents, (b) specific rotations, and (c) constituent sugars, and the results showed no marked difference in the chemical compositions of the polysaccharides. The hydrolysates of the pectin samples were found to contain degraded galacturans, D-galacturonic acid and its oligomers, varying amounts of D-galactose and L-arabinose and traces of D-xylose and L-rhamnose. Some of the samples of polysaccharides were fractionated by (a) column chromatography on diethylaminoethylcellulose (phosphate form) columns and (b) electrolyte precipitation with sodium acetate, sodium chloride and potassium chloride. The polysaccharide was eluted in a single broad band from diethylaminoethylcellulose and was found to contain all the sugars present in the original polysaccharide sample. The fractions obtained by electrolyte precipitation were analysed and showed no marked difference in chemical composition. The results of this fractionation have been discussed in this paper.

Citrus fruits are one of the chief sources of pectins. Similarly, turnip has been reported to contain appreciable quantities of this group of polysaccharides. The samples of pectins were extracted from these two sources in a stepwise manner with ethanol–water (80:20) to remove colouring matter and soluble sugars, with water to extract soluble polysaccharide(s), with ammonium oxalate solution to extract pectins as ammonium pectate and finally with EDTA solution to recover rest of the pectin still present in the plant material as calcium salt. Pectins are very susceptible to degradation under various conditions. They are easily degraded by acids, alkalis, enzymes and even in neutral solutions. This property of pectic substances presents a number of problems during extraction and fractionation of the polysaccharide. In view of this fact the polysaccharide samples were extracted under mildest possible conditions.

The samples of pectins were purified via insoluble calcium salt. Calcium chloride solution was added to a solution of polysaccharide and the precipitated calcium pectate after centrifugation was washed with water. The supernatant solution and washings were found to contain no neutral polysaccharide(s). Calcium pectate was converted to ammonium pectate by heating at 90°C with ammonium oxalate solution.

The analyses of the samples of pectins are given in Table 1, which shows that all the samples have similar uronic acid anhydride contents and specific rotations. Samples of the polysaccharides were hydrolysed and the hydrolysates gave the similar paper chromatographic pattern, indicating the presence of sugars shown in Table 1 in the approximate proportions given in paranthesis.

Fractionation

The samples of pectic substances were fractionated by two methods: (i) DEAE-cellulose column chromatography and (ii) graded precipitation with electrolytes.

(1) The homogeneity of samples of pectinic acids was examined by DEAE-cellulose column chromatography. All the polysaccharide preparations gave the same elution pattern on this ion-exchange resin. More than 95% of the polysaccharide was eluted in a single broad band with NaOH solution and only traces of polysaccharide were eluted with 0.5M sodium phosphate buffer and found to contain the same constituent sugars as the original pectinic acid.

(2) Various pectic acids have been fractionated by graded precipitation with electrolytes such as sodium acetate and potassium chloride and in some cases pure galacturonans have also been isolated.

Pectin samples were de-esterified to give pectic acids, under very mild conditions. Fractionation of these pectic acids by Bishop's method gave only one major fraction, which precipitated when the molarity of sodium acetate in the solution was 0.18. Traces of pectic acid were precipitated at lower concentrations of sodium acetate, and the analysis of these polysaccharide samples showed the presence of all the constituent sugars present in the original polysaccharide. Neither pure galacturonan nor neutral polysaccharide(s) was obtained.

Biological Sciences Section

CHEMICAL INVESTIGATIONS OF SEEDS OF ABRUS PRECATORIUS LINN

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Abrus precatorius Linn, is a shrub of the natural order Leguminaceae growing wild in the plains of India, Burma and other tropical countries. There are three varieties of it namely white or white with black spot, blank and scarlet.

The seeds are physiologically active and are useful in affections of nervous system, in skin diseases, ulcer and leprosy. Seeds contain a substance that produces local inflammation of conjunctiva. The oil from the seeds acts as an active antifertility agent.

Ghatak and Kaul reported that oil from it contained low percentages of free fatty acids, unsaturated acids and unsaponifiable matter but no hydroxy acid. The results obtained by Mandiratta and Dutt are in good agreement with those reported by Ghatak et al., however they reported higher percentages of free fatty acids and presence of hydroxy acids. Lefar et al. studied the oil portion in detail by gas-liquid chromatographic method.

The qualitative studies of the free amino acid have been made by Riaz and Khan. Recently Sharma et al. have studied the amino acid contents of seed protein.

The pectic substances of Abrus precatorius seeds were studied by Roudier and Orillard.

In the present work qualitative and quantitative estimations of free amino acids and carbohydrates present in the scarlet variety have been made and an attempt to isolate the biologically active component/components by simple method has also been made. The work on the active oil portions (four) is in progress in collaboration with the Physiology Department, University of Karachi, Karachi, and will be reported later.

**Experimental and Results**

The scarlet variety of seeds of Abrus precatorius Linn., 450 g, was extracted successively with petroleum ether, 80% alcohol and ammonium oxalate. An oil (sp. gr. 0.88) was obtained on removal of petroleum ether from its extract and phospho- or sulpho-lipids, mono-, di- and triglycerides, alcohols, sterols, free fatty acids and sterol esters were present. The oil was saponified and separated by repeatedly extracting the diluted mixture with ether. All ethereal extracts were combined, washed with water and dried (Na₂SO₄). After evaporating the solvent, the residue was dissolved in alcohol and subjected to fractional crystallisation when four products were isolated with m.p. 136–38, 122–24, 134–36, and 129–21°C. These gave positive tests for sterols and their IR spectra were studied. At least one of these products is expected to be biologically active. The amounts obtained were small and the structural work is now in progress with larger quantities.

**Saponifiable Portion.** From saponifiable portion free fatty acids were liberated on acidification with HCl. These were taken in alcohol and separated further by fractional crystallization; and were identified to be stearic (2.72%), palmitic (4.92%) and behenic (1.78%) acids.

**Alcoholic Extract.** The solvent was removed in vacuo and the material obtained (11.33 g) was treated with distilled water and heated up to 50°C when a soluble Sₖ (9.92 g) and insoluble SR₁ (1.41 g) were obtained. On keeping in refrigerator soluble portion SR₁ threw out a small quantity of insoluble material which was separated by centrifugation, when a soluble Sₗₐ and a residual portion SR₂ were obtained. The soluble portion Sₗₐ was subjected to ion-exchange chromatography for separation of amino acids and carbohydrates. The column was packed with activated resin Amberlite-IR120. Soluble portion was slowly applied on column and eluted with distilled water in order to separate carbohydrates from amino acids. Fractions of 10 ml each were collected at a rate of 50 ml/hr, using an automatic fraction collector. Forty-three such fractions were collected and treated for carbohydrates.

Fractions 3–15 gave positive tests for carbohydrates and their optical densities were observed at 365 nm. These carbohydrate fractions are concentrated and marked CF₁ (Fig. 1).

After separation of carbohydrates elution was made with 1% ammonia. Ten ml fractions were collected at the same rate. The concentration
ASSAY OF METHYL PARATHION AND FENITROTHION IN CROP EXTRACTS USING VAPOUR-PHASE SEPARATION IN CONJUNCTION WITH GAS CHROMATOGRAPHY

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Methyl parathion and Fenitrothion were separated and assayed by electron capture gas chromatography using stationary phase of 5% DC-200 on Celite at 180°C. Crop extracts contained substances which interfered with the gas chromatographic assay of these insecticides. Vapour-phase separation removed these interfering materials so that 0.1 p.p.m. of Methyl Parathion and Fenitrothion could be assayed in spinach, cabbage, apple, and potato and 1.0 p.p.m. in sugar-cane and cotton.

The organophosphorus compounds Fenithion \([O, O\text{-dimethyl}-O-(3\text{-methyl}-4\text{-nitrophenyl phosphorothioate})]\) and methyl parathion \([O, O\text{-dimethyl}-O-(4\text{-nitrophenyl phosphorothioate})]\) are widely used insecticides.

Although closely related, they differ much in their toxicity, Methyl Parathion being more toxic than Fenitrothion. It is, therefore, important to be able to distinguish between the two substances and to have a reliable and sensitive method for analysis of their mixtures.

The methods described to date do not distinguish between the two compounds. The colorimetric method of Averell and Norris and its subsequent modifications are based on the reduction of the nitro group to amino group by zinc powder with the formation of the diazo derivatives and coupling with \(N\text{-}(1\text{-naphthyl})\text{ethylenediamine}\) measuring the colour formed by absorbance at 555 nm. The method can be used for either of these insecticides separately but because both of them give a similar colour the method cannot be used for mixture of the two. The alternative polarographic method is based on the reduction of nitro-group to amino-group at the cathode and is also unsuitable for the analysis of the mixture because the half-wave potential of Fenitrothion is \(E_h=-0.58\) V, almost the same as the half-wave potential of Methyl Parathion \((E_h=-0.55\) V) when a Kolthoff buffer \((\text{pH}=5.0)\) is used.

The two compounds may be distinguished by IR spectrophotometry but the method lacks sufficient sensitivity to measure residual quantities.

Gas-liquid chromatography is powerful method for separating substances but no suitable system has been described which may be used for distinguishing and determining Fenitrothion and Methyl Parathion together. But extracts of various plants often contain materials which interfere with gas-liquid chromatographic assay. Thus, an effective method, for separating the compounds from coextracts, is also needed for general use. Many methods have been described for clean-up based on selective adsorption, solvent partitioning and other physical and chemical methods. Each is efficient and useful for a particular problem but they lack general application. Of all the methods adsorption column chromatography is probably the most widely used but the disadvantage of this technique is that it provides variable recoveries. Farrow reported a vacuum-sublimation clean-up method but the method also gives variable recoveries. Gunther et al. described a vapour-phase clean-up adopted and modified in turn by Storherr and Watts and also Kim et al. to obtain improved recovery and wider application.

This paper describes a gas chromatographic method for separating and assaying Methyl Parathion and Fenitrothion, and its use in conjunction with a vapour-phase clean-up apparatus (Fig. 1) built in this laboratory to separate Methyl Parathion and Fenitrothion from substances extracted from plants which interfere with the gas chromatography of the two insecticides.

**Experimental**

*Material and Methods*

Separating funnel 250 ml capacity; rotatory film evaporator; nitrogen high purity, oxygen free; sodium sulphate anhydrous, Analar grade; acetone redistilled fractionally; n-hexane redistilled fractionally; chloroform Analar grade.

All the solvents were fractionally redistilled in all-glass apparatus at least once to remove traces of impurities which effect electron capture detectors and interfere with the assay of pesticides. Each redistilled solvent was checked for impurities by gas-liquid chromatography of a 5 μl sample from 30–50 ml of the solvent concentrated to 0.1–0.5 ml.

Standard stock solutions of 1 mg/ml of both Methyl Parathion and Fenitrothion in n-hexane

*From Rothamstead Experimental Station, Harpenden, U.K. under U.K. Colombo Plan.*
CAROTENOID CONTENT OF CITRUS FRUITS

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Carotenoid content of peels, flesh and juices of eight citrus fruits have been determined. Feutrell's Early has been found to be the richest source. Higher percentage of carotenoids resides in the peels than in the flesh, which contains carotenes either in equal or greater amounts than the former. Peels possess more saponifiable carotenoids (xanthophyll esters) than flesh. The distinct redder appearance of red blood is due to pigments other than carotenoids as its carotenoid content is less than that of others. The spectra of the carotenoids of peels and flesh of all varieties except lemon and grape-fruit are similar but different from those of pure β-carotene.

Investigations on the carotenoid content of green plants, dehydration of alfalfa and preparation of carotenoid and chlorophyll concentrates have been reported earlier.\(^1\)-\(^3\) The yellow-orange colour of citrus fruits\(^4\)-\(^7\) is also due to carotenoids. Many of these compounds, in addition to being useful and desirable food colours, are precursors of vitamin A. Pakistan produces about 4.7 lakh tons of citrus fruits per year.\(^8\) Citrus peels—an industrial waste—may be a rich source of carotenoids, pectin and oil due to their abundant availability. It was, therefore, considered advisable to study the carotenoid content of different indigenous citrus varieties, with a view to utilizing the citrus peels for the production of carotenoid concentrate for its use as colouring, flavouring and vitamin A fortification of foods. No attempt was made to separate and identify the carotenoids here.

**Experimental**

**Material and Apparatus**

Commercial solvents such as deactivated alumina (Merck)\(^4\) were used. Beckman DK2A and Unicam spectrophotometers were employed.

**Procedure**

Fruits purchased locally were hand-peeled, and peels and flesh (pulp) were worked up separately. Peels were chopped and thoroughly mixed to make a composite sample. Similarly, a composite sample was prepared from flesh. Juice was extracted with juice extractor from the flesh of different fruits and filtered through a two-fold muslin cloth separately. A definite weight (10 g) of each of peels, flesh and juice was extracted with 1:1 mixture of petroleum ether and acetone. Carotenoids and carotenes were estimated in terms of β-carotene as described earlier.\(^3\) Carotenoid concentrate can be prepared by removing the solvent under reduced pressure. The results have been recorded in Table I. The spectra of the total carotenoid solutions of peels and flesh of kinow, lemon, grape-fruit and β-carotene have been recorded in Fig. 1.

**Fluorescence Studies**—The fluorescence was observed under UV light by chromatographing the total carotenoid solution on alumina column using light petroleum as the eluent.

**Partition Test**—Measured volume (25 ml) of total carotenoid solution was shaken with an equal volume of 90% methanol in a separating funnel. Epiphasic layer was washed with 90% methanol until no further pigments were extracted.
BIOSYNTHESIS OF PORPHYRINS BY BACTERIA

Synthesis of Porphyrins From 8-Aminolaevulic Acid by Cell-free Lysate of Micrococcus colpogenes

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The results of the synthesis of porphyrins from 8-aminolaevulic acid (ALA) by the whole and lysed cells of Micrococcus colpogenes are presented. Whereas the lysate metabolized ALA at a rate faster than the whole cells, the amount of coproporphyrin formed by it was much less than the amount formed by the cells. Under aerobic incubation the lysate formed mainly uroporphyrin. Anaerobic incubation of the lysate resulted in marked increase in the formation of coproporphyrin, but the ratio of coproporphyrin to uroporphyrin formed by it was still less than the ratio of the porphyrins formed by the whole cells. Porphyrins with intermediate number of carboxyl groups between uroporphyrin and coproporphyrin were detected only in the case of incubation mixture containing the lysates. The difference in the metabolic operation of the pathway due to the difference in the organization of a system has been discussed.

The effect of metal ions on the synthesis of porphyrins from ALA by cells of M. colpogenes was reported earlier.1 This paper describes the ability of the cell-free lysate of the bacteria to synthesize porphyrins from ALA.

Extracts of animals, plants and microorganisms have been shown to convert ALA to porphobilinogen (PBG).2 Enzymic conversion of PBG to porphyrins including protoporphyrin has been demonstrated to occur in the presence of cell-free preparations from Chlorella3 and Euglena,4 spinach leaf and wheat germ,5 and other materials.6 Among the bacteria, cell-free extracts of the Gram negative bacteria, Rhodopseudomonas spheroides7 and Hæmophilus sp.,8 have exhibited enzymic activities responsible for the formation of porphyrins up to coproporphyrin from ALA. Townsley and Neilands9 have demonstrated the synthesis of porphyrins from ALA by lysate of the Gram positive bacteria, Micrococcus lysodeikticus. Their study was concerned, mainly, with the types and amounts of porphyrins formed by lysates made from the organisms cultivated on medium containing 'low' and 'adequate' iron levels.

The present study gives a comparative account of porphyrin-synthesizing ability of intact and lysed cells and presents evidence of the importance of 'organization' of cellular components within an organism in the regulation and smooth operations of normal metabolic processes.

Experimental

Materials.—The reagents and the strain of M. colpogenes used in the study were the same as described in the previous paper.1

Methods

Growth and Harvesting Conditions of the Bacteria.—

The organism was grown and harvested as described earlier.1

Preparation of Cell-lysate.—Cell lysate was made by the treatment of cells with lysozyme essentially by the method of Salton and Champman.10 Cells were suspended in 0.1m potassium phosphate buffer, pH 7.5, and lysed with Armour Laboratories, crystalline egg-white lysozyme (100 μg lysozyme/ml of cell suspension containing 8–10 mg/ml of dry wt bacteria) at 30°C. Under these conditions lysis of cells occurred in approximately 1 hr. Unlysed cells, if any, and cell debris were separated by slow centrifugation. The supernatant represented cell-free lysate.

Incubation of reaction mixtures (see the text) and oxidation of porphyrinogens formed in the mixtures followed the method described in the previous paper.1 Incubation under vacuum was carried out in 50 ml Thunberg tubes. For the study of the amounts and types of porphyrins formed at different periods of incubation, the incubating vessels were taken out from the shaker at intervals, and placed directly into crushed ice and subsequently frozen at -10°C.

Fractionation and Determination of Porphyrins.—Porphyrins present in the reaction mixtures were fractioned and determined by the method of Dresel and Falk.11 Since very little protoporphyrin is formed by the bacterial system under the conditions of incubation, coproporphyrin was extracted from ether with 5% HCl in all the experiments. The amounts of uroporphyrin and coproporphyrin in 5% HCl (w/v) separately were calculated from the expressions described by Cornford.12

Chromatography.—Samples of porphyrins were identified by the ascending chromatographic method of With13 on Whatman paper No. 1. Chromatograms were developed in dark room at ambient temperature for 90 min, dried and
COMPARISON OF GAS CHROMATOGRAPHY COLUMNS FOR PESTICIDE RESIDUE ANALYSIS

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Four column packings, 10% DC-200 or 15% QF-1 on 80-100 mesh celite and mixtures of the two, were tested for electron-capture gas chromatographic assay of 25 insecticides or alteration products. Detection of insecticides on the 15% QF-1 column was usually more sensitive than on 10% DC-200 column and relative retention times on the two columns differed.

A packing made by mixing equal amounts of celite coated with 10% DC-200 or 15% QF-1 more nearly resembled the 15% QF-1 packing than the 10% DC-200 packing. A second packing of similar composition made by mixing the silicone polymers before applying to celite more closely resembled the DC-200 packing but generally detection was less sensitive.

Since the retention times on the columns differ they provide additional ways of identifying and separating insecticides.

To distinguish pesticide residues by their retention times, most gas-liquid chromatographic analyses utilise a stationary phase of a nonpolar methyl silicone polymer such as DC HI-Vac grease, SE-30, DC-200, DC-11, SF-96. These versatile stationary phases separate a large number of pesticide chemicals but they all chromatograph similar degree of separation. In general the reasons for choosing any of these phases in preference to another are minor. DC-200 has been used in our laboratory for gas chromatographic assay of chlorinated pesticides and several organophosphorus compounds but it is well known that chromatographic analysis by a single system gives only a tentative identification which must be confirmed in at least any other system. Gas chromatography is a most convenient method for analysis of pesticides and it was desirable to have an alternative gas chromatographic system.

A number of liquid phases other than DC-200 have been tried to change order of elution or effect different separations. Retention times and response data are available for organophosphorus pesticides on silicone-type columns used mainly for the analysis of chlorinated hydrocarbon pesticides. Epon-1001 and QF-1 have been used by some laboratories, but the number of pesticides they will chromatograph well is limited. Goulden et al. have reported the use of five columns, each with a different liquid phase, Beroza and Bowman reported the relative retention times of 25 organophosphorus insecticides on three silicone columns and on a diethylene glycol succinate column. McCully and McKinley tested 6% QF-1 and 4% SE-30 mixed prior to application to chromosorb-W for use in residue analysis, and demonstrated the potential value of mixtures of liquid phases for the gas-chromatographic separation and confirmation of the identity of pesticides residues. More recently Watts and Storherr reported the use of the mixture of QF-1 and DC-200 on Gas chromatograph for the analysis of organophosphorus pesticides residues, and Burke and Holwade reported its use for chlorinated compounds.

This paper describes the investigations of the retention times and sensitivity of detection of chlorinated and organophosphorus insecticides using column of QF-1 and DC-200 both alone and mixed together on celite in gas chromatography equipment available in this laboratory.

Experimental

Apparatus.—A Philips gas chromatograph Model PV-4000 Series, equipped with an electron capture detector, was used with high purity nitrogen as carrier gas at 25 lb/in² giving a gas flow of 40 ml/min. Stock solutions of 1 mg/ml of pure insecticides (Table 1) were prepared in n-hexane, stored in all-glass-stoppered bottles in a refrigerator. Dilutions were made as necessary.

Columns.—To compare different types of column packings, columns were prepared with either 15% QF-1 or 10% DC-200 coated on to celite as stationary phases and with mixtures made in two different ways. One mixed column (A) was prepared by mixing equal amounts of supports treated with 15% QF-1 and with 10% DC-200. A second mixed column (B) contained the same quantities of QF-1 and DC-200 but it was prepared by mixing the liquid phases together before application to the solid support.

The silicone polymers were dissolved in chloroform and 80-100 mesh celite was added to give a slurry in a round-bottomed flask. The solvent was evaporated by warming in a water bath at about 60°C while the flask was rotated to ensure a uniform coat of polymer on celite. The dried coated solid was air-elutriated to separate the
The relative toxicity of the three insecticides, gamma-BHC, Bromophos and Carbaryl varies from one species of insect to another. These insecticides were tested against five species of insects A. domestica, T. castaneum, P. americana, B. germanica and C. analis. Results showed that all the three insecticides are about equally toxic to A. domestica and T. castaneum but against C. analis gamma-BHC is much more toxic. Bromophos is the most toxic insecticide against B. germanica. Against P. americana gamma-BHC, is about three times as toxic as Bromophos and Carbaryl.

The present work is intended to demonstrate the relative toxicity of gamma-BHC, Bromophos and Carbaryl to five species of insects (Periplaneta americana, Tribolium castaneum, Blatella germanica, Acheta domestica and Callosobruchus analis) because no information on this aspect under conditions prevailing in Pakistan was available.

The three insecticides used belong one each to chlorinated hydrocarbons, organophosphate and carbamate groups. In the first group, gamma-BHC was selected because it is being produced in Pakistan. From the other two groups Bromophos and Carbaryl were respectively selected because of their quite low toxicity to mammals. The safety factor is important because the insects selected for the present evaluation are generally found in households and relatively safe insecticides are desirable for their control to avoid hazards to human beings. The reason for using these insects was their notorious ability to survive under adverse conditions of humidity and temperature and scarcity of food. Studies on the relative toxicity of some insecticides to the boll-worm and tobacco bud worm were reported by Brazzel et al. The response of the various instars of the boll-worm and tobacco bud-worm to DDT and Endrin applied topically was reported by McPherson et al. Gast and Treece who compared the susceptibility of the face fly Musca autumnalis and the housefly M. domestica using a microapplicator. Soliman determined the toxicity of gamma-BHC and DDT to H. ochraceus (Brun) by topical application and found BHC more effective than DDT. Hamilton found LD₅₀'s for Aldrin against resistant larvae and adult of Western corn root-worm by microapplicator. Lemon evaluated in the laboratory Malathion, Bromophos and Fenitrothion for use against beetles infesting stored product by means of topical application technique. Leigh et al. compared the topical toxicity of chlorinated hydrocarbons, organophosphates and carbamate insecticide and found that chlorinated hydrocarbons as a group were less effective than the other two groups of compounds compared; probably due to population resistance to most organochlorine insecticides.

Material and Methods

Tests Insects.—P. americana and B. germanica were reared on wheat bran, T. castaneum on wheat flour and A. domestica on wheat flour mixed with fish meal. C. analis was raised on gram at 30–35°C and 50–70% R.H.

Treatment of Insects.—Test insects of known age were inactivated by cooling to −5°C before treating individually with measured drops of an acetone solution of insecticide from an Arnold hand microapplicator. 1–2 day-adult C. analis and 1–2-month old adult T. castaneum were treated with 0.5 μl of insecticide solution applied to ventral side of the thorax. 2–3-month old A. domestica and 5–7-month old nymph of P. americana were treated with 1.0 μl and 3–5-month old B. germanica with 0.5 μl of insecticide solution at the base of coxa of hindleg.

P. americana were kept in petri dishes and A. domestica in 100-ml glass beakers closed with muslin. The other three species of insects were kept in 2½ × 1 in tubes covered with muslin held in place with rubber bands. Three batches of insects were used for each treatment. Controls, both untreated and treated only with the solvent alone, were used concurrently in each test. The tubes, dishes and beakers containing the test insects were kept in large glass jars (18 × 8in) immersed in a constant temperature water bath maintained at 30°C ± 1°C as no alternate constant temperature facilities were available. This arrangement became necessary when it was observed that variations in temperature affected the toxicity of pesticides used. Preliminary tests were made with insecticide solutions with the concentrations differing by a factor of 10. Then five concentrations differing by a factor of 2 were used to determine the LC₅₀ of each insecticide. Each test was repeated at least three times. All the three insecticides were tested at the same time
STUDIES ON THE RESIDUAL TOXICITY AND VAPOUR ACTION OF PETKOLIN-M

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Biological tests using T. castaneum, Callosobruchus analis and Periplaneta americana show that the toxic action of Petkolin-M as a residual film persists longer in closed than in open containers and it also persists longer against T. castaneum and C. analis than P. americana. A toxic vapour action of Petkolin-M was deduced and confirmed in tests which showed that vapour action against P. americana persists longer than T. castaneum and C. analis. It is concluded that Petkolin-M is a mixture of at least two toxic substances, one more toxic as a residual film to C. analis and T. castaneum and the other more toxic as a vapour to P. americana.

In quest to save foreign exchange by developing indigenous resources for pesticide manufacture, PCSIR produced the insecticide Petkolin-M by chlorination of various low boiling cuts of petroleum waste. A wide range of biological activities, including toxicity to various species of insect of these substances have been reported in a series of publications. Lack of investigations of the residual and other related properties of these compounds prompted the present study of residual action of Petkolin-M reported to be the most promising of the three Petkols. This paper describes tests of the residual toxicity of Petkolin-M both in covered and open containers. Marked differences of effectiveness and length of action of the insecticide suggested that it might also be effective as a fumigant and examination of this hitherto unexplored property of Petkolin-M is also described in this paper.

Experimental

Materials and Methods

Test Insects.—Periplaneta americana, Tribolium castaneum and Callosobruchus analis were reared in the laboratory at 25–35°C and relative humidity 60–80%.

The cockroaches were reared on a mixture of wheat bran and yeast with water supplied to them from a glass tube fitted with a loose cotton-wool plug. These insects were 6–9 months old when used for test.

C. analis were reared on whole gram. 4–8-day old adult beetles were used for tests. T. castaneum were reared on wheat-flour. The adults were used for tests when they were 10–30 days old.

Handling of Insects.—For both residual and fumigation tests the cockroaches were immobilised by chilling at 0°C for 15–20 min because unchilled insects were too active and escaped whilst being transferred to the test containers. Other insects did not need inactivation for handling. Brush was used for transferring the insects other than P. americana.

Toxicity Tests.—The treatments were replicated in all the tests. Three batches of 10 adults each of T. castaneum and C. analis were always used. For residual assay 5 batches of 5 P. americana were used but for fumigation tests only 3 batches of 5 insects were used.

Residual Film Action.—Two kinds of residual film tests were made by exposing insects to filter paper circles impregnated with Petkolin-M; one in the open or ventilated and the other in closed containers.

Circles of filter paper (6 in and 4 in dia) were impregnated by spreading evenly from pipette 2.0 ml of 2.0% Petkolin-M in n-hexane solution. The papers were dried at room temperature for 5 min. Each treated paper was tested for toxicity when dry and then at intervals by releasing fresh insects on the same papers in the same dishes. Tests with closed containers were made twice weekly but with open containers tests were made daily because of the short residual action. All these tests were made at room temperature and humidity during the months of March–June. During this period the means of temperature was 25–35°C and humidity was 60–90%.

Petri dishes of 6 in dia were used as closed containers for all the three species of insects. Because C. analis are small, active, can climb clean glass and squeeze through small spaces, it was necessary to put weights on the tops of dishes to prevent escaping.

Beakers of 4 in dia (500 ml) were used as ventilated containers and were covered with muslin, held in place by rubber bands so as to prevent the escape of P. americana and C. analis which can climb on glass.

Vapour Action.—The vapours from portions of Petkolin-M in air-tight containers were tested for toxicity by exposing all the three species of insects at intervals until 24-hr exposure no longer killed them. C. analis and T. castaneum were exposed in presence and absence of food but P. americana were tested only in the absence of food. At first insects were exposed twice weekly but because of the small toxicity in the presence of food the test
Preliminary Screening Tests of Antifertility Compounds Inhibiting the Reproduction in Housefly, Musca Domestica (L.)

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Sterilization of male can in certain circumstances be more efficient than killing as a method for control of insects. A number of chemicals (chemosterilants) show promise of producing sexual sterility in insects without some of the practical limitations of radiation. The present publication encompasses the result of screening of 42 compounds produced by PCSIR Laboratories. The results obtained indicate that three compounds affected the reproductive potential of housefly appreciably. They are β-dimethylaminopropiophenone hydrochloride, 3,4,5-trimethyl benzamide and acid from iodothalantin.

The preliminary studies reported herein were initiated to find out a few effective compounds for inhibiting the reproduction of housefly, Musca domestica (L.). The results obtained indicate that out of a group of 42 compounds, three compounds are very effective while 12 are moderately effective.

In each test 20 pairs of newly emerged adult houseflies were released in wire screen cages fitted with narrow-mouth test tubes, containing water to increase humidity in the range of 60–75% R.H. The temperature ranged between 80–85°F. The compounds were given orally at the dose of 50–100 mg/g food (glucose) for 3 days. After 3 days, the flies were examined to determine mortality caused by the chemicals. The dose was decreased in case of high mortality. The flies were fed on untreated food consisting of dry milk to provide sufficient proteins essential for egg development. Beside milk protein 6% sugar solution soaked in cotton was also supplied. The cotton pieces soaked in milk also served as oviposition medium. This medium was made available to 3-day old treated flies to lay eggs and replaced daily for 21 days. The eggs laid per cage were collected on moist filter papers for observing percentage hatch and the time required for hatching of the affected eggs. The oviposition was noted for a period of 3 weeks, which was considered to be the life span of the treated flies. Cages containing untreated food were used as check. In experiments herein reported, the treatment was replicated three times. These methods are with certain modifications over the technique described by Fye et al. and Fye. Since both the sexes were given antifertility compounds, the results did not demonstrate whether sterility, if it occurred, had been induced in males, females or both. The percent control of reproduction potential was calculated by applying the following formula:

\[
\text{Control of reproduction} = \frac{100(V_1 - V_2)}{V_1} \times 100
\]

where \(V_1\) is the number of viable eggs per female in a control and \(V_2\) is the number of viable eggs per female in test treatment.

The results obtained with 42 compounds at the dose of 25–100 mg/g food are summarized in Table 1. The most effective compounds are β-dimethylaminopropiophenone hydrochloride, 3,4,5-trimethyl benzamide, which produced 85% control of reproduction at the dose of 50 mg/g and 100 mg/g, food respectively. Acid from Iodopallantin controlled 86% reproduction at 100 mg/g food. Twelve compounds proved moderately effective producing 70–75% inhibition of reproduction (Table 1). Compounds inhibiting reproduction below 70% are considered ineffective.

Table 2 presents the prevention of oviposition due to antifertility effect of the compounds. The compounds 3,6-dichloro-4-methylpyridazine at the

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Table 1.—Effect of 42 Compounds on the Fertility of Houseflies Fed for 3 Days after Emergence.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Concentration mg/g food (glucose)</th>
<th>Average No. of eggs laid (+)</th>
<th>No. of viable eggs (+)</th>
<th>% Control of Reproduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amudol</td>
<td>100 mg/g</td>
<td>95</td>
<td>71</td>
<td>50</td>
</tr>
<tr>
<td>N-skatyl-2-methylbenzimidazole</td>
<td>&quot;</td>
<td>89</td>
<td>76</td>
<td>47</td>
</tr>
<tr>
<td>N-skatylbenzimidazole</td>
<td>&quot;</td>
<td>56</td>
<td>45</td>
<td>61</td>
</tr>
<tr>
<td>Benzimidazole</td>
<td>&quot;</td>
<td>95</td>
<td>71</td>
<td>51</td>
</tr>
<tr>
<td>p-Nitrophenyl-β-dimethylaminopropionic acid</td>
<td>&quot;</td>
<td>87</td>
<td>43</td>
<td>70</td>
</tr>
<tr>
<td>β-Dimethylaminopropiophenone hydrochloride</td>
<td>50 mg/g</td>
<td>41</td>
<td>14</td>
<td>85</td>
</tr>
</tbody>
</table>

(Continued)
THE RESIDUAL TOXICITY OF PETKOLIN IN COMPARISON WITH PHOSALONE AND DDT

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The residual life of Petkolin, Phosalone [O,O-diethyl-S-(6-chlorobenzoxazolone-3-ylmethyl) phosphorodithioate] and DDT alone and Petkolin +15% Phosalone mixture was determined by using three to four-week old adults of red flour beetle, Tribolium castaneum (Herbst). At 90°F and a R.H. (relative humidity) of 55% ± 5% filter papers treated with Petkolin, Phosalone, DDT and Petkolin +15% Phosalone mixture remained toxic for 4, 4, 161 and 28 days respectively. Petkolin was compatible with Phosalone in the present formulation and the residual life of the mixture was longer than that of both the component insecticides.

The environmental conditions play an important role on the residual life of insecticides. Results reported by other workers indicate the importance of physical factors of the environment in relation to residual life. Sweetman1 reported that temperature in the range of 90°F–102°F with high humidity conditions decreased the residual life of DDT. Burgess and Sweetman2 also reported similar findings. Teotia and Dahm3 reported that high temperature and low humidity shortened the residual life of a number of insecticides more than low temperature and high humidity.

Keeping in view the results of residual toxicity of insecticides reported by the above workers in different environmental conditions, the present investigation was undertaken to determine the residual life of Petkolin, Phosalone (Zolone) and DDT at 90°F and 55% ± 5% R.H. in the laboratory by using Tribolium castaneum (Herbst). A mixture of Petkolin +15% Phosalone was also included for the residual evaluation as the same formulation was being tried for its compatibility and efficacy against different pests of field crops.

Procedure

The test insect used was red flour beetle, Tribolium castaneum (Herbst) which was reared in the insectary as described by Peterson.4 Three to four-week old adults were used throughout the period of evaluation.

Two test dilutions of each of the three insecticides and one mixture were made in acetone. To test the persistence of the insecticides 1 ml of acetone solutions of the insecticides were spread evenly on 9 cm circles of No. 1 Whatman filter papers. Two concentrations were used for each insecticide, 2% and 5% for Petkolin and DDT, and 7% and 10% for Phosalone, and a solution of 15% Phosalone in Petkolin. In all 16 papers were treated, two with each concentration of each insecticide. The filter papers were kept in petri dish halves and were dried for 24 hr in the same laboratory in which the bioassay was made. After drying, the treated filter papers were kept in marked petri dishes which were placed in a desiccator whose humidity was adjusted at 55% ± 5% R.H. by saturated solution of calcium nitrate. The desiccator was kept in a constant temperature cabinet maintained at 90°F ± 2°F.

For each test 40 beetles (3–4 week old) were exposed for 3 hr to each of the 16 treated filter papers. Following exposure, the beetles were transferred to clean petri dishes and held in the laboratory for 24 hr after which the mortality counts were made. Mortality was recorded daily for the first seven days in all the cases. Then once a week in the cases of Petkolin, Phosalone and Petkolin +15% Phosalone mixture and at intervals of 3 weeks in the case of DDT. Acetone check and untreated control were also kept with each set of the experiment and the mortalities were corrected by using Abbott's formula.5 After each test the filter papers were returned to the desiccator to be stored in the controlled temperature cabinet till the time of next exposure.

Results

The residual toxicities of Petkolin, Phosalone and DDT alone and a mixture of Petkolin +15% Phosalone stored at 90°F and 55% ± 5% R.H. diminished at different rates.

Petkolin.—The Petkolin-treated papers were toxic for only 4 days. Papers treated with 2% Petkolin killed 50% of the insects in the first test, 30% on the 4th day but only 10% on the 5th day (Fig. 1). Similarly the toxicity of papers treated with 5% Petkolin decreased from 85% on the first day, 61% after 4 days and to only 10% after 5 days (Fig. 2).

Phosalone.—The toxic effect of Phosalone like that of Petkolin persisted for 4 days, though in this case the loss of toxicity of residues was not gradual. In the residues of 7% dilutions no mortality was noted on the 5th day as compared to 70% mortality the day before (Fig. 1). Similarly, the toxicity of the papers treated with 10% Phosalone...
The fungicides used against common pathogenic fungi are fairly soluble in water. These fungicides, however, cannot be used against fungal attack especially in high rainfall areas where wood and other building material, in major part of the year, is exposed to high moisture conditions and the fungicide from paints etc. tends to be washed-off fairly soon after application. In these investigations 50 metallic cyanurates in their primary, secondary and tertiary forms have been evaluated in Sabourad's petri dish. Direct spore inoculation as in the original method because agar did not solidify rapidly at room temperature, allowing the insoluble cyanurates to settle at the bottom of petri dish which gave erroneous results. A thick spore suspension of Aspergillus niger was prepared in sterile water at 30°C and 0.01 ml of this suspension was centrally inoculated in each petri dish. Direct spore inoculation or agar control plates was used with secondary and tertiary cyanurates of cadmium and mercury was found effective in 0.1% concentration. The secondary and tertiary cyanurates of copper, and primary, secondary and tertiary cyanurates of nickel and lead inhibited A. niger at 0.5% concentration. The fungicidal action of all these cyanurates was tested by toxic agar diffusion method.

**Material and Methods**

For screening the primary, secondary and tertiary cyanurates of calcium, zinc, nickel, tin, cobalt, barium, magnesium, antimony, copper, chromium, lead, mercury, iron, cadmium, thoriun, sodium and ammonium, toxic agar diffusion method was used. The primary, secondary and tertiary cyanurates of the above metals have been designated as la, 1b, lc, 2a, 2b, 2c and so on respectively.

The test compounds were compared with zinc oxide. The concentrations of zinc oxide used in the experiments were 0.020, 0.030, 0.040, 0.050, 0.060, 0.080 and 0.10% of the active ingredient.

A few cyanurates were tested at random for determination of a general toxic range. The concentrations of the toxic compounds used in this experiment, ranged from 0.01 to 1% with a difference of 0.01% in each successive dilution. The concentration range from 0.02% to 1% was found suitable for evaluation of fungicidal properties of all cyanurates. In subsequent experiments, method of Ashrafi et al. was used with certain modifications. The different concentration of all test compounds were the same as used for zinc oxide and were prepared in 20 ml of Sabourad's agar, instead of 15 ml agar as reported in the original method. These toxic agar plates along with nontoxic Sabourad's agar control plates were kept at 10°C for 1 hr instead of at room temperature as in the original method because agar did not solidify rapidly at room temperature, allowing the insoluble cyanurates to settle at the bottom of petri dish which gave erroneous results. A thick spore suspension of Aspergillus niger was prepared in sterile water at 30°C and 0.01 ml of this suspension was centrally inoculated in each petri dish. Direct spore inoculation or agar control plates was used with secondary and tertiary cyanurates of cadmium and mercury was found effective in 0.1% concentration. The secondary and tertiary cyanurates of copper, and primary, secondary and tertiary cyanurates of nickel and lead inhibited A. niger at 0.5% concentration. The fungicidal action of all these cyanurates was tested by toxic agar diffusion method.

**Results**

The compounds which did not permit the growth of Aspergillus niger in Sabourad's agar at 0.1%conc and above were termed 'highly toxic' the compounds which were effective in inhibiting the growth of Aspergillus niger at 0.5%conc and above were termed 'medium toxic' and the compounds which did not check the growth of the test fungus at 1% concentration were termed 'least toxic'.

It was also noted that at 0.08% conc of primary copper cyanurate, the growth of Aspergillus niger was wrinkled, raised and suppressed. At 0.06% concentration of cadmium cyanurates, the growth of Aspergillus niger was highly suppressed with a translucent halo round the growth after 8 days of inoculation. The cyanurates of mercury suppressed mycelial growth and sporulation at 0.06% concentration.

The primary cyanurate of copper and primary, secondary and tertiary cyanurates of cadmium and mercury were found to be 'highly toxic' (Table 1). The most effective compound was 12b which inhibited 96.7% growth of the test fungus at 0.06% concentration in comparison with the control. Comparing the fungi toxic action of
Metabolic pathways of the insecticide Carbaryl (1-naphthyl N-methylcarbamate) have been reported in mammalian tissues, their liver microsomal fractions, insects and certain higher plant species.\(^3,5,7\) The detoxication of Carbaryl yields both the hydrolysis products such as 1-naphthol as well as certain oxidation products. Boush and Matsumura reported the metabolism of carbaryl by an obligate symbiote Pseudomonas melophthora (Allen and Rikker) of apple maggot.\(^2\) Production of 1-naphthol and a polar unidentified metabolite were recognized. The potential of microorganisms, in general, to metabolize organic compounds particularly when they are adapted to them has been expressed.\(^1,12\)

A bacillus Pseudomonas phaseolicola (Burkholder) and a fungus Aspergillus niger (Van Tieghem) were used. Both were isolated from local soil and the cultures were maintained in these Laboratories. The microorganisms were incubated with the carbamate and after appropriate time the incubation mixture was subjected to extraction by chloroform. The organosoluble fraction was purified and analyzed by column and thin layer chromatography and a colorimetric procedure.

### Materials and Methods

*Pseudomonas phaseolicola* was grown in peptone broth and was standardized by an optical density method. 100 ml of the suspension was incubated with 100 mg of Carbaryl at 37°C with constant shaking 5 ml aliquots of this mixture were drawn at 0, 1, 2, 6, 24 and 48 hr, each aliquot extracted twice with 5 ml of chloroform, dried (Na\(_2\)SO\(_4\)) and evaporated at room temperature. The extract was analyzed as to the amount of 1-naphthol in the mixture. Each extraction was treated with 1 ml of 6% methanolic acetic acid followed by 0.5 ml of 1% methanolic p-nitrobenzenediazonium fluoborate. The naphtholic colour thus developed was read at the wavelength of 485 nm (adapted from Miskus \textit{et al.}^9). In another experiment the bacilli were homogenized by ultrasonic vibrations in MSE instrument at 1.75 amp and then exposed to Carbaryl. For chromatography purposes the bacillus culture was allowed to metabolize the chemical for 18 hr because this time provided metabolites sufficient for further clean-up process. It was then extracted with chloroform as indicated above. Because of the tissue interference, direct thin layer chromatography was not feasible. Silica gel column of 1.5 x 30 cm was used. The elution was performed with the following solvent system in the listed order: hexane 50 ml, 1:1 hexane–ether 100 ml, ether 50 ml and methanol 50 ml. Ten ml fractions of the eluate were collected from the column. Portions of these were subjected to 1-naphthol analysis, formaldehyde analysis\(^4\) and thin layer chromatography. For TLC, 4:1 ether–hexane solvent system and silica gel G plates were used. In order to identify naphtholic derivatives on the chromatograms, fluoborate reagent was used after spraying the plates with 15% potassium hydroxide.\(^9\) The chromogenic portions of silica gel adsorbent on these plates were scraped with a metallic blade and extracted separately into methanol. The methanol extracts were read in a colorimeter at the wavelength of 485 nm.

*Aspergillus niger* was grown in the Czapek’s media and exposed to Carbaryl in distilled water. Similar procedures as above were observed. Efforts to break the spores were not successful.

### Results and Discussion

In the studies involving *P. Phaseolicola*, the production of 1-naphthol increased over a period of 48 hr. At one hour of the incubation, 2 \(\mu\)g equivalent of Carbaryl per sample was found as 1-naphthol; at 2 hr 4.5 \(\mu\)g, at 6 hr 10.5 \(\mu\)g at 24 hr 270 \(\mu\)g and at 48 hr 310 \(\mu\)g of the 1-naphthol were produced. On column, 1-naphthol eluted mostly in the hexane fraction and was identified by IR spectra and thin layer chromatograms. Based on TLC some of the unmetabolized Carbaryl appeared in the hexane fraction and the rest in the next solvent fraction. Except for methanolic

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ROTENONE AND ITS USE IN ERADICATION OF UNDESIRABLE FISH FROM PONDS

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Rotenone, its origin and use are described. Results of application of the chemical to three ponds of the Fish Seed Multiplication Farm at Jamalpur, Mymensingh, for eradication of undesirable species are given. Rotenone takes time to reach the deep bottom of ponds in absence of any effective agitation of water. It was observed that snakes, frogs and crustaceans are not readily affected by this plant derivative as they can escape the action through terrestrial respiration. A list of fishes and other aquatic organisms in order of their susceptibility to rotenone is presented. A concentration of 1.0 p.p.m. at summer temperature, around 30°C in this region, was found adequate to kill fishes.

In pond management, piscicide is used for removal of undesirable species and thinning out excessive fish population due to rapid reproduction. Piscidal action is preferred to dewtering and drying of pond bottom because the latter process is uneconomic and may result in loss of fertility of the pond. Rotenone is a widely known piscicide. It is a white compound \((C_{24}H_{29}O_6)\) extracted mostly from plants of family Leguminosae. According to Gunther and Jeppson\(^3\) the important genera are Derris, Lonchocarpus, Milletia, Mundulea and Tephrosia. Derris grows in the Far East. Two species, Derris elliptica and Derris malaccensis are cultivated. Lonchocarpus are found in south and central America. Ong\(^4\) states that Tephrosia is widely distributed in Africa, Australia, Asia and North America. Rotenone was first isolated from a Derris species in 1902 and named 'Rohten'. Subsequently the compound was extracted from the same and some other sources. Gunther and Jeppson\(^3\) further state that different species of plants in their different parts contain different concentrations of active material. Greatest single attribute of rotenone is its specificity to fish when used in recommended dosage. According to Rounsefell and Everhart\(^5\) rotenone is apparently harmless to plants and higher vertebrates in usual dosage and the affected fish is not rendered inedible. Bennet\(^6\) states that a concentration of 0.5 p.p.m. of derris powder with 5% rotenone should be lethal to fish. However, experience with market products has shown that it is risky to depend upon a dosage of less than 1 p.p.m. to give a complete kill of fish. Rounsefell and Everhart\(^5\) further state that rotenone is more lethal at higher temperature and have been found ineffective below 48°F. The chemical is somewhat more toxic in acid than in alkaline water. Toxicity is more quickly lost in hard, alkaline water than in acid soft water. The chemical has not yet found wide use in fishery management in this country. Not much work on the application of the chemical for pond management and other fisheries investigation has been reported. The present study was undertaken to determine the dosage of rotenone necessary for eradication of undesirable species and also to find out susceptibility of different indigenous species to this plant derivative.

Materials and Methods

Rapid multiplication and excessive growth of miscellaneous fishes, particularly *Tilapia mossambica*, have been impeding the production of the Fish Seed Multiplication Farm ponds at Jamalpur in the district of Mymensingh. Three ponds of the farm were selected for rotenone treatment with a view to complete eradication of the fish population. Emulsifiable cube root containing 5% rotenone, 11% other cube extracts and 84% inert ingredients, manufactured by Chemical Insecticide Corporation, New Jersey, U.S.A., under the trade name Chem. Fish Special O.F. was used at concentrations 1.0 p.p.m., 1.5 p.p.m. and 2.0 p.p.m. respectively on the 22nd and 23rd of May, 1970. The ponds had the original numbering 2, 4 and 5. Methods described by Rounsefell and Everhart\(^5\) and Swingle\(^6\) have been followed. All the ponds were of rectangular shape. Hence, the area was determined by taking average measurements of length and width through the waterline by a 100-foot measuring tape. Average depth was estimated by taking at least 3 depth readings from different parts of the ponds with the help of a bamboo pole. Volume of water in each of the pond was estimated from the area and average depth. Requirement of rotenone for the desired concentration was calculated. The desired quantity of rotenone was weighed in a small container by a spring balance. The measured rotenone was then poured into a steel drum where it was liquefied with water. The mixture was then spread over the surface water in the ponds. Wind direction at the time of application of the chemical was taken into consideration and care was taken that no amount of the piscicide is lost due to wind.
INTRODUCTION OF NEW TERMINOLOGY IN THE SKELETON OF THE FISHES BELONGING TO THE ORDER HETEROSOMATA (PLEURONECTIFORMES)

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A detailed osteology of the flat fishes (Heterosomata) shows false orbit locating the migrated eye. The term pseudoorbit is suggested for such a false orbit. The five families of the order Heterosomata have the characteristic feature of possessing the pseudoorbit. A detailed study of the pseudoorbit in each family shows variation in the surrounding bones forming the boundary of the pseudoorbit.

Kyle and William stated that the juvenile flat-fishes bear the two eyes on either side of the chondrocranium; during metamorphosis one eye migrates to another side, assuming a characteristic feature of two eyes on the same side. The migrated eye is lodged in a bony socket formed by a somewhat rounded gap between the two frontals. This bony socket does not fulfil the conditions of an orbit which is usually made up by the frontals at the dorsal surface, parasphenoid at the ventral surface, aliphenoid or basisphenoid at the posterior surface, and lateral ethmoid and vomer at the anterior surface. In case of flat-fishes the migrated eye lies in a socket formed by the frontals on the lateral and posterior sides, parasphenoid at the floor and lateral ethmoids at the anterior side. These bones altogether form a false orbit for the location of the migrated eye. The term pseudoorbit is here assigned to such a false orbit. The present paper deals with the term pseudoorbit and its variations in the families of the order Heterosomata or Pleuronectiformes.

Materials and Methods

The material studied include the chondrocrania of the families Psettodidae, Bothidae, Pleuronectidae, Cynoglossidae and Soleidae.

As specimens of family Pleuronectidae have not been recorded from the Arabian Sea they were obtained from the National Museums of Canada in Ottawa through the courtesy of Dr. D.E. McAllister. They are, <i>Lyopsetta exilis</i> NMC65-200, <i>Platichthys stellatus</i> NMC64-683-E, and <i>Reinhardtius hippoglossoides</i> NMC64-756.

The other fish specimens studied were collected from Karachi harbour, and include: (1) <i>Psettodes erumei</i>; (2) <i>Pseudorhombus arsius</i>; (3) <i>Synaptura orientalis</i>; (4) <i>Cynoglossus sindensis</i>.

Specimens of small sizes were stained in alizarin red according to Holister's method. Large alcohol preserved specimens were boiled in KOH to remove the flesh and were treated with hydrogen peroxide to clarify different sutures. The crania were finally stained with alizarin. Diagrams have been made with a proportional divider and are enlarged 2–4 times from original size of the specimen; photographs were reduced half the length of the sketches.

Discussion

At the early developmental stage of an eye a hollow outgrowth the 'optic vessel' is given off from each side of the forebrain. It project out further and touches the ectoderm at the sides of the head. This ectoderm becomes thickened and invaginates. Eventually, it forms a closed sac and is separated from the rest of the ectoderm. During the development of the chondrocranium, cartilaginous investment is formed around the optic capsules. The cartilaginous investment takes the shape of an orbit in the adult stage.

The eye in an orbit is moved by six muscles, four of these arise from the inner wall of the orbit and pass to their insertion over the equator of the eye. One of them is dorsal, the superior rectus; a second ventral, the inferior rectus; a third anterior or internal rectus; and the fourth the posterior or external rectus. The two remaining are superior and inferior oblique muscles arising from the anterior region of the orbit and inserting into dorsal and ventral surface of the eye ball.

Gregory describes the orbit in these words: "the adult teleost endocranium is a complex of four intergrading parts surrounding the orbits; these may be named ethmovomer block, the interorbital bridge, the cranial vault, and the keel bone or parasphenoid". Thus the orbits are the two excavations anterior to the auditory region, lying on the lateral sides of the cranium. They are bounded by the frontals at the roof, parasphenoid at the floor, vomer and lateral ethmoids at the anterior end, while the alisphenoids or basisphenoids form the posterior boundary.

Osteological studies on the fishes of the order Heterosomata revealed that an abnormal condition exists for the socket of the migrated eye. The migrated eye is lodged in a bony socket formed by a gap between the two frontals and the circumorbital bones are also absent. A pseudomesial bar is present running between the two
COMPARATIVE STUDIES OF PROTEIN BANDS OF HAEMOLYMPH AND FAT BODY OF THE COCKROACH, BLABERUS CRANIIFER (BURMEISTER.)

Part IV.—Eggs*

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Egg proteins were recovered by homogenization and extraction of oothecae with distilled water. Water-soluble proteins were separated by paper electrophoresis. The number of well-defined bands varies from one to four. B and I is coincident in eggs, haemolymph and fat body.

Electrophoretic studies of proteins from haemolymph and fat body of a species of cockroach, Blaberus craniifer, were undertaken in all the stages. This paper deals with egg extracts. Among earlier studies of this nature papers by Laufer1,2 alone refer to egg proteins. He compares them with blood proteins of adults.

Materials and Methods

For collection of eggs the females were anaesthetized and their abdomens slightly pressed to expel oothecae. All egg samples were collected at random with regard to age, stage of development or protein content. This procedure had to be adopted because complete embryonic development takes place inside the body of the cockroach and hatching takes place immediately after egg deposition.

Distilled water was used as a solvent. Egg samples were ground in a homogenizer for two to three minutes. As in the case of the fat body three layers resulted: the sediment, supernatant, and a top lipid layer. Supernatant was withdrawn below the lipid layer.

Procedure of electrophoresis was the same as already reported by Cheema and Garthe.3

Results and Discussion

The number of well-defined bands varies from one to four, though sometimes a fifth band also has been seen (Figs. 1 and 2).

Bands I and IV have the greatest spread, and least concentration while II and III are the narrowest but most well-defined. In some cases bands III and IV are of the same width and II is the narrowest. Occasionally band IV is the most intense. In all samples examined band I remained the widest. Comparison with female haemolymph shows that band I is comparable in both, but is slightly wider in eggs (Fig. 1).

When the egg is compared with female fat body, and both have five bands, then band V is of the same width and coloration in both (Figure 2). Bands II, III, and IV are all narrow and only two of these coincide. Band I of fat body gives the impression of being split into two.

Variations from the above in major and minor bands are not infrequent. This could be explained as possibly due to different stages of de-

*Part of the thesis presented by A.A. Cheema to the Graduate School, Northern Illinois University, Dekalb, U.S.A. in partial fulfilment of the requirements for the Master of Science degree.
Nitrogen fixation by certain Azotobacter species is well established and its economic importance in the field of agriculture is now beginning to be realised. It has been estimated that about 25 lb of N₂ is fixed per acre annually by the nitrogen-fixing bacteria in the soil. Recently in the soil, use of bacterial fertilizers comprising bacterial inoculants particularly of Azotobacter species, and those of phosphorus-solubilising organisms, viz. Bacillus megatherium var. Phosphaticum, has been published principally in the U.S.S.R. and to some extent in other agriculturally advanced countries. In some cases, increased fertility of the soil was observed.

This paper reports results on the growth of Azotobacter vinelandii together with its nitrogen-fixing activity, both in soil and in liquid cultures.

**Fermentation Methods**

The culture Azotobacter vinelandii (Department of Agri. Chemistry, University of Sydney) is maintained in Winogradsky medium having the composition of K₂HPO₄, 0.5 g; MgSO₄, 0.0125 g; NaCl, 0.0125 g; FeSO₄·7H₂O, 0.005 g; MnSO₄·4H₂O, 0.005 g; Na₂MoO₄·4H₂O, 0.005 g; and water 1 l. To this salt solution 1% sucrose or 2% molasses is added. The temperature for growth is maintained at 30°C and pH 7.2.

Inoculum is prepared by growing the organism in 100 ml Erlenmeyer flask, containing 25 ml sterilizing medium. After shaking for 24 hr, the culture is transferred to 300 ml Erlenmeyer flask containing 100 ml sterilized medium and shaken for another 24 hr. It is again transferred to 5-l flask, containing 3 l medium and aerated through glass wool column, again for 24 hr. This is finally fed into 40 l medium, contained in a 50-l glass bottle for growing large scale culture. During growth, samples were taken out for microscopic examination and for the determination of total sugar, fixed nitrogen, pH, dry weight and growth rate of cells. The concentration of sugar was maintained at 1% level by periodic addition of the sterilized sucrose or molasses solution, during fermentation.

Nitrogen determination was made by micro-Kjeldahl method and sucrose consumption by iodometric method. Total dry weights were obtained by centrifuging and washing cells from 100 ml of the fermented medium and drying at 95°C to a constant weight. Growth rate was determined by measuring turbidity at 660 μm Unicam Spectrophotometer at 8 hr interval.

Nitrogen Fixation in the Soil.—About 2 kg of soil, moistened with water was placed in three wooden trays, at a temperature around 32°C, in such a way that the thickness of the soil was about 1 in. Fresh cultures of Azotobacter were introduced by mixing the cell suspension with the soil, so that, the initial population was 10⁸ bacteria/g of the soil. Soil was aerated by stirring daily and nitrogen contents determined after 15 days interval.

Field experiments were conducted in three experimental fields of the dimensions 4 ft × 10 ft. Field No. 1 was inoculated with the freshly grown culture of Azotobacter vinelandii and weekly sprayed with 2% solution of molasses for a period of 8 weeks (about 8 kg). Field No. 2 was weekly sprayed with 2% molasses but no culture was introduced. Field No. 3 was weekly sprayed with water only, and acted as control. Soil was always stirred before spraying culture molasses or water. Field studies were conducted from September to November 1969.

**Results and Discussion**

Table 1 shows that in the growth medium, with sucrose as carbon source, after 16 hr of growth, 7.9 mg of nitrogen was fixed per 100 ml of the medium. The fixation was 10.2 mg/100 ml after 24 hr and after 32 hr, 14.105 mg of nitrogen/100 ml was fixed. Beyond 32 hr there was no increase in the nitrogen fixation.

The value of 14.05 mg N/100 ml is considerably lower than that of 32 mg N/ml reported by Sylvan and Burris with their strain of Azotobacter vinelandii. In a large number of experiments carried...
Allium cepa (piyaz or onion) is very commonly used throughout the world and specially in India and Pakistan, as a condiment in daily cooking and as a vegetable salad; but very few people realize that it has many useful medicinal properties. Recent findings about its beneficial effect in heart troubles have revived a great interest and investigations are going on in Pakistan and many other countries to find out the constituents responsible for its beneficial effects. In this article an attempt is made to bring out the medicinal properties of onion and to give a review of the chemical, pharmacological and clinical investigations carried out so far.

Allium cepa (Liliaceae), onion or piyaz, is a bulbous, biennial herb, bearing linear, hollow, fleshy, cylindrical leaves and umbels of small white flowers. The flowers mature into 3-celled capsular fruits containing small, black seeds. The flower heads also, sometimes, bear bulbils. The underground bulbs, which constitute the crops, vary in size, colour (white, yellow, red, brown), shape (round, flat, conical), firmness, keeping quality, period of maturity and strength of flavour. It is cultivated throughout the world in tropical and subtropical countries and is grown from seeds, bulbs or bulbils.

Onions are largely used as an article of food and condiment. These are often eaten raw, flavoured with lemon juice, pepper, salt, etc., to enable the body to get the maximum amount of the vitamins, minerals and other useful constituents present. Mostly the onions are used as condiment after roasting, in which case the vitamins, volatile constituents, etc., are destroyed. The medicinal properties of onion are mostly destroyed after roasting. Bulbs are useful in fever, dropsy, catarrh fevers, they are eaten twice a day with two or three black peppers, with remarkable relief. Roasted onions mixed with cumin, sugar candy and cow's ghee is a nice demulcent of great benefit in piles.

Chemical Constituents of Onion

Two Colombian varieties of onion have the following composition: Moisture 87.46–87.77, fat 0.26–0.37, proteins 1.03–1.63, sugars 5.45–6.04, cellulose 1.30–1.50, pectin 2.0–2.16, mucilage 2.61–3.38, allyl isothiocyanate 1.50–1.59, total ash 0.492–0.741, acid sol. ash 0.344–0.521, sodium and potassium 0.1128–0.1028, iron 0.00083–0.0015, calcium 0.04234–0.0736%, and traces of cobalt and copper. These also contain vitamin B35–50%, and vitamin C, 0.91823–1.01853 mg/100 g. The individual sugars are arabinose 1.0%, rhamnose 0.69%, xylose 0.67%, ribose 0.45%, glucose 2.05%, fructose 0.20%, sucrose 3.23% and polyfructosan 1.45%. Also present are malonic acid (0.5 mg/g of fresh material) malic, citric acid and propionaldehyde.

Onions contain a precursor identical to allin (+)-S-allyl-L-cysteine sulfoxide, which is responsible for releasing pyruvic acid enzymatically in the fresh juice of onions. The bulbs contain p-cumaric acid, caffeic acid and ferulic acid. The coloured outer skin contains quercitin(I), spiraeoside(II) (quercitin-4-mono-D-glucoside), protocatechuic acid(III), phloroglucinol (IV) phloroglucinol carboxylic acid(V) and pyrocatechol(VI) besides two unknown quercitin glucosides m.p. 224–26°C(VII) and m.p. 196–8°C(VIII): fleshy onion scales contain I,II,III, IV,V,VI, VII, VIII and ferulic acid, while leaves contain I,II, ferulic acid and caffeic acid.

Gas liquid chromatography of its steam-volatile fractions gave 16 different peaks, out of which Pr2S2, MeSSPr and Me2S2 were identified. Onion juice contains MeCHO, EtCHO and MeCH2CH=CH2 which were identified as dinitrophenyl hydrazones. The three varieties
SHORT COMMUNICATION
BIOLOGICAL SCIENCES SECTION


THE FATTY ACIDS OF INDIGENOUS RESOURCES FOR POSSIBLE INDUSTRIAL APPLICATIONS.
PART II. – INVESTIGATION OF SOME SPECIES OF BORAGINACEAE FAMILY

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PCSIR Laboratories, Lahore 16
(Received July 2, 1970; revised January 22, 1971)

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MORPHOLOGICAL VARIATIONS IN MUNG (PHSEOLUS AUREUS) INDUCED BY GAMMA IRRADIATION

MUSHTAQUE AHMED RAJPUT

Radiation Genetics Institute, Lyallpur
(Received April 13, 1971; revised May 1, 1971)

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THE INFLUENCE OF RAINFALL ON THE POPULATION OF NEMATODES IN BANANA FIELD

MANZOOR SAEEED AND SHAHID H. ASHRAFI

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SOME OBSERVATIONS ON BREAKING EXTENSION PERCENTAGE AND TENACITY OF WHITE JUTE (CORCHORUS CAPSULARIS)

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(Received December 12, 1970)
UTILIZATION OF CORN-SUGAR IN CANNED VEGETABLES

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(Received September 1, 1970; revised November 24, 1970)

The effects of corn sugar (Cerelose brand) on the colour properties, texture qualities and flavour acceptability of five different canned vegetables were studied. Canned vegetables were processed with brine solutions containing various proportions of sucrose and Cerelose at two different levels of sugar solids (2.5 and 5.0%). Measurements of drained weight, texture and colour were made after the equilibration of the canned vegetables at 40°F and 90°F for various periods. The drained weights and shear press readings of certain vegetables were increased when corn sugar was used in the brine. Hunter colour values L (lightness), aL (redness) and bL (yellowness) of all the vegetables were affected when sucrose was replaced by dextrose in the brine. Dextrose caused slight to moderate effects when used at 25% replacement of sucrose and greater effects when used in quantities up to 100% replacement. The flavour of the canned vegetables was affected but little by the presence of dextrose in the brine.

Corn sugars are used extensively in canned fruits and fruit products. However, a relatively small amount of corn sugars are used in processing canned vegetables. Relatively little is known about the effects of corn sugar solids on the qualities of canned vegetables.

During the past few years new types and kinds of corn sugars are available. In view of this, a study was undertaken regarding the use of corn sugar (Cerelose brand) dextrose for processing canned vegetables. The object was to study the effects of corn sugar on the colour properties, texture qualities and flavour acceptability of canned vegetables.

Review of Literature.—Fellers et al.¹ reported the satisfactory use of dextrose in canned peas, beets and tomatoes. Canned sweet corn containing added dextrose became dark in colour and had a poor flavour. Dextrose was used advantageously in sweet pickles.

Elckelberg²,³ indicated that up to 50% replacement of sucrose by dextrose in canned peas and canned beets was acceptable. The use of Cerelose brand dextrose, reported by Fabian and Pivnic,⁴ as replacement of sucrose up to a certain percentage, did not affect consumer's acceptability of pickles.

Lopez et al.⁵ indicated that the addition of dextrose contributed to the normal flavour of sauerkraut.

Tigg⁶ reported on the use of two different corn syrups and dextrose as a partial replacement of sucrose in canned peas. A small difference in sweetness of peas packed with corn syrup and with sucrose was noted.

Experimental

Processing Vegetables.—Five different vegetables—peas, sliced beets, lima beans, cut yellow wax beans and whole kernel corn were processed with two different series of sugar solutions consisting of proportions of sucrose/dextrose. The vegetables were processed in the commercial lines at different canneries in Wisconsin, U.S.A.

The corn sugar used for processing vegetables was Cerelose brand dextrose. Carefully weighed lots of canned vegetables were processed for determination of drained weights.

Sweeteners.—The compositions of the solutions used as brines and added to the canned vegetables prior to processing are shown in Table 1.

For vegetables other than corn, two types of sugar brines were prepared, containing sweeteners at the rate of 2.5 and 5.0% sugar solids. For whole kernel corn, sweeteners were used containing 5.4 and 7.0% solids respectively. Salt was added at the rate of 2.0% in the brine solution for peas, beets, lima beans, 1.0% in the brine for wax beans and was omitted for whole kernel corn. Measured amount of brines were added to the cans by a 'Flotron' dispenser prior to the addition of the vegetables.

Measurements.—The drained weights of the canned vegetables were measured according to the Almanac.⁷ The texture of the canned vege-
A STUDY OF THE PROFILE DISTRIBUTION ON MANGANESE IN SOME SOILS OF EAST PAKISTAN AND ITS PEDOGENIC SIGNIFICANCE

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(Received October 21, 1970; revised December 19, 1970)

This communication deals with the translocation and concentration of manganese in the soil profiles from a 'hilo' topographic area in East Pakistan. A higher proportion of manganese was present in the free oxide form in the soils of uplands compared to that in the lowland soils. Of all forms of manganese only soluble manganese was found to be influenced by vegetative cycle. Pedogenic significance of the vertical and horizontal distribution pattern of manganese in these soils has been discussed.

Manganese occurs to the extent of 1250 p.p.m. in igneous rocks which constitute around 95% of the earth's crust. In sedimentary rocks, however, the amount of manganese varies from 1000 p.p.m. in shale to less than 200 p.p.m. in sandstone. But in soils manganese is mostly known as an element important for plant growth and soil fertility. As a result, a vast literature exists regarding its uptake by plants and its availability in soils. Little work has been reported about the behaviour of manganese during pedogenic reorganisation of soil parent materials. Pedological importance of manganese and its movement in soil was first emphasized by Fujimoto and Sherman in some tropical soils. Recently few more works have been reported.

It is known that a portion of manganese present in soils occurs in certain ferromagnesian minerals and other complex silicates. Manganese is reported to occur also in secondary layer silicates in which this element usually occupies a place in the octahedral layer by isomorphous replacement. Some of these minerals are so insoluble that they may not be readily decomposed even by concentrated acids and, therefore, are not considered to be 'available' manganese in soils.

The two forms of manganese in soils which are thought to be important as the source of this element for plants are replaceable manganese, and manganese dioxide that may readily be reduced to divalent manganese on flooding a soil. Bohn reported that the concentration of Mn²⁺ increased in soil suspension which differed widely from those calculated by previous models of manganese behaviour. He derived an equation of pH–pMn for expressing the equilibrium solubility of MnO₂ in soil suspension.

Many authors worked on the chemical behaviour of manganese on flooding a soil. Conner found a significant increase in the amount of replaceable manganese after flooding a soil. Schollenberger also reported that submerged soils in which strongly reducing condition prevails are characterised by increased amount of divalent manganese content. Piper and Adams tried to correlate the amount of Mn²⁺ in soils with their redox potentials.

The precipitation of manganese from soil solutions has been an important source for the occurrence of manganese concretions in soils, manganese present in concretions are mostly oxidised and chemically inert. Leeper classified the manganese in soils into three distinct forms which exists in an equilibrium with each other. His classification may be presented as follows:

Manganese manganese⁰ Collodial hydrated MnO₂ (Soluble) (Slightly soluble) (Insoluble) MnO₂

Dion and Mann studied the manganese cycle in soils on the basis of oxidation—reduction equilibrium between the divalent and tetravalent manganese oxides and reported the existence of a trivalent manganese in soils which undergoes dismutation to give rise to divalent and tetravalent manganese.

In this paper the distribution of manganese in some well-drained and imperfectly drained soils of East Pakistan has been discussed with reference to their pedogenic significance.

Materials and Methods

Six soils profiles were collected from an area of undulating topography in the district of Sylhet in East Pakistan on natural horizon basis. The hills and hillocks of Sylhet are the outliers of the main ranges that surround this district from the north and south. The parent materials of these soils were ferroginous sandstone and were of mixed origin. The deposition of these sediments and their subsequent upheaval into hills and valleys took place during the late Tertiary Period. The area wherefrom the present soil samples were
PETROLOGY OF THE TERTIARY COASTAL SECTION AT COX'S BAZAR

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(Received August 29, 1970; revised December 19, 1970)

Petrographic and mineralogical studies of the coastal sections of Upper Miocene sediments at Cox's Bazar have been carried out. It is suggested that the sediments have been derived predominantly from a metamorphic source area. Further it is concluded that the sediments were laid down under shallow water condition probably in a shelf zone.

The area investigated lies 3½ miles south of the seashore town of Cox's Bazar, a subdivisional head-quarter situated 95 miles southeast of Chittagong (Fig. 1) The area is composed of hills of varying topography running along the coast of Bay of Bengal. The highest point in the area is 270 ft above sea level. These hills terminate abruptly against the seashore and expose beautiful sections of Tertiary rocks in the form of vertical cliffs trending NNE-SSW. The height of the cliffs along the beach varies within a narrow range of 115 ft–175 ft. Behind the cliffs exposures are scanty because of thick vegetation covering the hills.

Outcrop and Lithology

The succession (Fig. 2) has been worked out mainly on the basis of study of sections along the cliff. The whole succession is composed of similar rock types. Sandstone comprises approximately three fourth of the total rock exposed. Ripple marked siltstone and shale are found to be inter-bedded with sandstones. The whole sequence has, therefore, been tentatively named as Cliff Sandstone.

A thin fossiliferous marine intercalation has been found in the coastal cliffs indicating an Upper Miocene age for the sediments1 which makes the sequence equivalent of Tipam Series of the Assam.2 Rocks considered to be equivalent of Tipam on lithologic analogy from other areas in East Pakistan have been reported.3

The sandstones exposed are found to be yellowish grey, semiconsolidated and highly cross-bedded at the base of the cliff with concentration of dark minerals along the false bedding. Presence of carbonized woods in the sandstone has also been noted. The features like cross-bedding and concentration of dark minerals are totally absent from the sandstones in the middle and upper parts of the section.

Petrography

Method of Study.—For petrographic studies eight samples of sandstone, three from cross-bedded sandstone at the bottom, three from sandstone beds lying below the fossiliferous bands but above the cross-bedded sandstone sequence and two from sandstone beds lying above the fossiliferous bands, have been studied. Laboratory investigation has included (a) size analysis by dry sieving after necessary disaggregation using Tyler standard sieve screens of 16, 32, 60, 115 and 200 mesh, (b) heavy mineral separation from -200 sieve fraction by centrifuging, and, (c) microscopic determination of the heavy minerals and their relative abundance on the basis of grain counts.

Fig. 1.—Map showing the location of sections measured at points A, B, C, D, E, F, G and H.

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THE TITANIUM CONTENT IN REPRESENTATIVE SOILS OF A PLEISTOCENE TERRACE IN EAST PAKISTAN AND ITS PEDOGENIC SIGNIFICANCE

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(Received October 21, 1970; revised January 5, 1971)

Titanium in soil, silt and clay fractions of a number of soils from the Barind tract was determined. The mean TiO₂ content in the soils ranged from 0.6 to 1.2 per cent with a mean value of 0.8% per cent. The per cent TiO₂ in the clay fraction was higher than that in the silt fraction. These soils showed signs of the development of argillic horizons.

In the crust of the earth titanium is thought to be the most abundant of all the trace elements. Goldschmidt estimated the average titanium content in the igneous rocks to be 0.44%. Rankama and Sahama collected data on the content of titanium in the sedimentary rocks. Their results showed that most of the sedimentary formations contained an average of 0.5% titanium. These authors further reported that the Quaternary clays of Norway had only 0.47% titanium. From the above information it appears that in most igneous and sedimentary formations the titanium content ranges from 0.4 to 0.5%. In latosols and latosolic soils, however, the amount of titanium is much higher. Rankama and Sahama reported a laterite having a titanium content of 3.25%. Jackson indicated that not all laterites contain high titanium in them. In a study of the Hawaiian soils Sherman reported that titanium in these soils ranged from 2.5 to 25%. In this study the above author was dealing mostly with latosols developed on freely drained highlands. In a recent study of the gray hydromorphic soils of the Hawaiian Islands it has been reported by Hussain that these imperfectly drained soils in Hawaii have as low as 0.6% titanium.

Titanium is present in all soils but their amount depends on the quantity of this element in the parent materials and parent rocks.

A number of authors have worked on the movement and subsequent accumulation of titanium during the pedochemical weathering of soil parent materials. Joffe and Pugh reported that titanium tends to accumulate in the surface horizon of laterite and podzol soils and indicated that titanium was possibly present as the mineral ilmenite. Hough and Byers also reported that titanium in soils was present as the minerals ilmenite and rutile and assumed that these were primary minerals and were resistant to chemical weathering. Later studies by Sherman have shown that the titanium mineral in the soils which were studied by Hough and Byers was present as anatase, a secondary titanium oxide mineral.

Sherman investigated the genesis of titanium-rich soils of the Hawaiian Islands and reported that titanium content was higher in the surface horizons of soils which developed under a humid tropical climate having an alternating wet and dry season. He further indicated that titanium easily dehydrated near the surface to form concretions and coated the surfaces of soil aggregates and peds. Katsura et al. worked with the titanium bearing iron oxides in some Hawaiian latosols which they designated as titanomaghemite formed by the direct oxidation of titanomagnetite without any subtraction of iron from the system or addition of titanium into the system.

Karim made a study of the pedological significance of titanium in some soils of South Australia and concluded that under lateric process of soil formation titanium content is lower in the A horizon clay than that in the B horizon clay and under podzolic process the titanium in the A horizon clay is higher than that in the B horizon clay. Robinson and Holmes pointed out that in the soils of the United States the titanium in the colloid fraction showed an opposite distributional trend to that of the soils.

First work on the titanium distribution of some soils in East Pakistan was reported by Karim and Khan. Their results showed an enrichment of this element in the colloid fraction of B horizons in the soils of the Madhupur tract, a Pleistocene terrace in East Pakistan. Their results further indicated that the distribution of TiO₂ in the soils followed the same trend as that of the clay fraction.

The Pleistocene terraces in East Pakistan are regarded as the relatively stable and older geologic formations of this province. Since pedogenic processes have been operative there for a considerable length of time the soils in these terraces have developed well-defined profile characteristics and the minerals have in some cases been segregated. The objective of the present study was to examine the profile distribution of titanium in the soils developed on a Pleistocene terrace in East Pakistan and to look into their pedogenic significance. In this report only the soils of the Barind tract, the largest of the Pleistocene terraces in East Pakistan have been considered.
The bast fibres such as ramie, hemp, flax and jute, in which the tiny cellulose ultimates are embedded in a cementing matrix including hemicelluloses, lignin and pectin, can be classed as two-phase materials.1 The existence of a two-phase structure within the cortex of wool has also been suggested.2

The strength of such composite materials where the cellulose units are very short (in case of jute it is 2-5 mm) must be determined largely by the extent to which the cementing materials i.e. lignin and hemicelluloses are capable of cementing them together. Some work has been done on the possible contribution of the cementing materials i.e. lignin and hemicelluloses of jute fibre on its tensile properties both in dry and wet conditions, but the subject is still a matter of conjecture.3-4 5

Failure and rupture mechanism of composite structures is very complex, it depends on various properties of the individual constituents, and the condition under which the fracture has occurred. It is of considerable interest to study the fracture mechanism of jute fibre, both from the technological view point and structural considerations.

**Experimental**

**Materials.—**A superior quality (Pak White Special) jute (C. Capsularis) was used for this study. Sample was taken from the mid portion of the strand and the individual fibres were combed out and finally by zoning method a numerical sample was drawn.

**Methods.—**The linear density (fineness) of the individual fibre was determined by weighing 10 cm length of fibre in a sensitive torsion balance. All fibres were conditioned at 20°C and 65% R.H. from dry state at least for 48 hr and tested under these conditions. Stress-strain properties were measured on an Instron Tensile Tester with a 5 cm test length and four different rate of extensions, 0.2, 0.5, 1.0 and 3.0 cm/min. At least 100 fibres were tested for each group. The stress-strain curves were plotted following Meredith’s construction6 and the initial Young’s modulus was calculated at 0.5% extension.

An optical microscope was used for studying the fractured ends of the fibres and the diameter of the fractured point.

**Results and Discussions**

The stress-strain properties of jute at different rate of strain i.e. 0.04, 0.10, 0.20 and 0.60 cm/cm/min at standard condition are reported in Table 1. It will be seen that the specific stress (tenacity) and initial Young’s modulus increased with the increase in rate of strain. For example, on increasing the rate of strain by 15 times the specific stress increased by about 36% and initial Young’s modulus by 41%. The breaking extension practically remained unaltered with the increase in rate of strain. The linear nature of stress-strain curve for raw jute fibre suggests that the breakage of the fibres occurs within the elastic limit, and Hook’s law of elasticity is roughly applicable in any part of the curve.2 Though the increase in strength and modulus of jute fibre with the increase in rate of strain is very high compared to other textile fibres, it is not surprising at all considering its very little extensibility, (jute 1% compared to 10-15% for other textile fibres) orientation factor and composite structure of the jute fibre.

When a fibre is subjected to an unaxial stress it breaks at its weakest point.8 Once an ultimate cell of the jute fibre is broken, the possibility of a catastrophic failure increases due to concentration of stress pattern at the edge of the broken ends. It is interesting to note that the probability of a clean cut or a catastrophic failure or breaking of all ultimates at a particular point increased with the increase of rate of strain and conversely the chance of slippage or the pulling out of ultimates proportionately decreased.

After the fibre is broken in tensile tests the broken ends of the fibres were examined under the microscope.

<table>
<thead>
<tr>
<th>Rate of strain cm/cm/min</th>
<th>Linear density (tex)</th>
<th>Specific stress (gf-tex⁻¹) S.E.</th>
<th>Initial modulus (gf-tex⁻²) S.E.</th>
<th>Extension at break (%)</th>
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CHEMICAL MODIFICATION OF THE CRIMP STRUCTURE OF WOOL FIBRE AND ITS EFFECT ON FELTING AND COMPRESSION

MUMTAZ AHMAD KHAN

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(Received August 26, 1970; revised October 28, 1970)

The crimp structure of wool fibre was modified by treatment with phenol-formaldehyde and the helical configuration became sinusoidal, resulting in increase in felting and decrease in compressional load. No change, however, took place in the crimp form of Merino wool (sine form) and, therefore, felting behaviour or compressional load remained unaffected. The possible factors which influence felting have been discussed and it was found that crimp form is the main factor affecting felting. The relationship between felting and compressional load has been established and shown to be mainly due to crimp form. The mechanism of felting was best explained by a modification of Martin's theory.

Considerable work has been done on yarn and fabric for rendering wool shrink-resistant. Little work seems to have been done, however, on the modification of crimp structure of wool fibre, except that by Crewther and Dowling who demonstrated that the removal of crimp enhances felting, while coiling of wool fibre retards it. They have, however, not studied the fibre characteristics other than crimp which could possibly affect felting. Recently, it has been shown that crimp form is the main factor concerned in changing the felting and compressional behaviour of purified raw wool. The present work was undertaken with the following objectives:

1. To modify the crimp structure of wool differing in crimp form by chemical means and to study the various factors which affect felting behaviour.
2. To study the bulk compression of wool and its relationship to felting, compression and crimp form.
3. To surmise modifications, if any, to the theory of felting.

Materials and Methods

Wool Sample.—In the preliminary experiments, a number of wool samples with different crimp configuration were used and finally the following two extreme crimp configurations were selected.

1. Dorset Horn (Helical).
2. Ryeland (Helical).
3. Merino (Sine).

The tips of the staples were removed and the wool thoroughly washed with diethyl ether, ethyl alcohol and distilled water, hand-carded and all vegetable matter was removed. The bulk was randomized in order to minimize sampling differences.

Single Fibre Properties.—The single fibre properties such as friction, diameter, stress-strain were measured by the usual methods described elsewhere. The measurements were made at 65% R.H. and 21°C.

A fibre rotator was used to measure the form of crimp (score) i.e. whether it was of sine or helical form. In practice, the crimped length, crimp frequency, crimp amplitude and straight length are measured. The straight length is then compared with the theoretical straight length for a fibre with similar wavelength and frequency, obtained from graphs, prepared separately for both helical and sine form equations. An arbitrary value of the crimp form (score) is given by: Score = S - S0 / S0; where S = experimental straight length; S0 = theoretical straight length from...
FACTORS AFFECTING THE SOFTNESS OF SILK-WOOL FABRICS

MUHAMMAD ASHRAF ALI

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For the purpose of estimating their tactile properties by means of hands and lips, 26 varieties of fabrics have been manufactured from different woolwefts which are plain-woven into the same silk warp. The lips test seems slightly more reliable than the hand test. In addition, the softness of the unrelaxed fabrics exhibits high positive correlations with their softness after wet-relaxation and felting. But the correlation between the softness of a fabric and that of its raw wool assembly is not very high because the former is additionally dependent on the variations of weave density, yarn evenness, tex, twist factor and ply number; besides, an interaction between twist factor and tex appears to modify the softness of the singles' fabrics. Nevertheless, the weft/cm alone accounts for 84.0% of the variations of fabric softness within their present ranges of variation.

The tactile sensation of textile materials is usually estimated by a subjective type of mild compression test in which a fibre assembly is squeezed by hands. The results are expressed in such words as soft, warm, lofty, crisp, firm, harsh, boardy, dead, lively, wiry, spongy, springy, lean, waxy, dry and muss-resistant. For example, the handle of Merino, Southdown and Lincoln wools are generally known as soft, spongy and harsh respectively. As discussed in man-made fibres, however, the wide variations of softness displayed by different fibres are largely attributable to their difference in substrate, which is evident from the large variations of their Young's modulus at 1% extension.

Fabric design, durability and price are often considered in trade situations but a fabric softness mainly determines the consumers' opinion of the fibre types. Because of its great significance in end-uses, the softness of handle mostly governs the buyers' preference for the apparel materials. This somewhat undefinable quality of a fabric is particularly desired in the dress materials of women and children. Hence, a definite knowledge of the factors determining the tactile property of a fabric could be of great interest to the manufacturers. Accordingly, this study purports to decipher the contributions of fibre, yarn and fabric qualities to the softness of handle manifested by a variety of silk-wool fabrics at different stages of their finishing.

Pure silk is, however, too costly for general use by the common people of East Pakistan. As a consequence, a stock of various silk clothes which are estimated at nearly rupees 9 lacs, has been left unsold during recent years at the lone silk factory of East Pakistan whilst its annual maintenance normally costs about rupees 2 lacs. Although the yarns produced in it are easily sold, sometimes by exporting the to West Pakistan, the stock of fabrics creates many economic problems such as those of idle capital, space and preservation in the factory. Thus it seems necessary to find additional uses for the silk fabric. Unfortunately, the uses of silk are limited by its rapid slackening due to high creep under the stress-strain of usual wear and tear. This difficulty may be overcome by suitable coupling of silk with wool because the latter normally exhibits felting shrinkage during any wet-cleaning. Such a blend may find outlets in the military dress materials where wool per se is highly valued. Thus a fabric of silk and wool fibres, both being nonflammable, may suit wide variety of end-uses, particularly, because it will possess certain desirable attributes which could not be developed by using any one of them alone.

Whilst silk is well known for highly desirable fabric handle and low filament friction, its handle mainly results from the supple filament characteris-tics. On the other hand, shrink-proofing of wool by alcoholic potash increases fibre friction and stiffness, and impairs its softness of handle. But the natural variation of fibre friction displayed by the wide variety of raw wools is rather small and practically independent of the large difference of their stiffness, therefore, the inferior handle of the shrink-resisted wools may arise from the increase of fibre stiffness and the resulting high resistance to bulk compression noted elsewhere too. This inference agrees well with the additional observation that the variation of loose wool compressibility is largely accounted for by the fibre diameter and crimp frequency which, in turn, govern the softness of handle. But an anomalous effect of crimp frequency can arise from visual bias if it is allowed to prevail upon the hand test of raw wools. Thus the softer handle displayed by the fabrics of relatively high-crimp wool tends to disappear on their wet-finishing that restores most of the fibre crimps removed by the processing stress. It, therefore, appears desirable to investigate the reproducibility and validity of the hand test when it is administered in presence of the visual bias for fibre crimp.

**Experimental**

The materials studied here comprised a mulberry silk of the multivoltine race commonly found...
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MOISTURE REGAIN AND CHEMICAL CHARACTERISTICS OF PAKISTANI WHITE AND YELLOW SILK

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