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THE QUENCHING OF TRIPLET STATES OF NAPHTHALENE IN SOLUTION
BY ELECTRON DONOR COMPOUNDS

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Naphthalene triplet decay rate constants in solution containing various electron donor compounds have been
made and the second-order quenching constants have been evaluated. A quantitative account of naphthalene triplet
quenching ability by various electron donor compounds is given in terms of relative height of the charge transfer
state.

Introduction

Considerable progress has been made during the last ten years in studies of the factor affecting
the $T_1 \rightarrow S_0$ radiationless transition. The work
so far done made it clear that certain second-order
processes are very efficient and photochemical
reaction of a molecule can be completely sup-
pressed by addition of a small amount of quench-
ing substance. The mechanism of such pro-
cess is of great importance in understanding the
problems concerned with photochemistry and
radiation damage in the solid and liquid state.

Different processes resulting in the enhancement
of triplet state decay rate by other molecules in the
ground or excited state have been experimentally
established. From flash-photolysis technique
point of view the important ones are:

1. Triplet-Triplet Annihilation.—It is the re-
sonance interaction between two like molecules in
their triplet state. The possible mechanism is

$$T_1^* + T_1^* \rightarrow S_1^* + S_0$$

$$S_1^* \rightarrow S_0 + h\nu$$

This process is responsible for delayed fluorecence
observed in certain systems.

2. Triplet-Triplet Energy Transfer.—It is a
collisional process resulting in the 'spin transfer'
from the excited molecule to the quencher mole-
cule and is not forbidden by spin conservation
rules, since it is only necessary that the total spin

momentum of the whole system be conserved
rather than that of each separate partner.

$$D(\text{triplet}) + Q(\text{multiplet}) \rightarrow D(\text{singlet}) + Q(\text{multiplet})$$

It is a necessary condition for this type of quenching
that the quencher $Q$ shall have a triplet level lower
than that of $D$.

3. Quenching by Paramagnetic Molecules.—This
involves the formation of a complex between an
excited molecule and a paramagnetic species,
followed by radiationless transition within the
complex, back to the ground states of the separated
molecules.

$$D(\text{triplet}) + Q(\text{multiplet}) \rightarrow D(\text{singlet}) + Q(\text{multiplet})$$

As the diamagnetic ions have no unpaired elec-
trons, there is no interaction between the spin
moments, each molecule must individually con-
serve spin momentum and no change will occur.
For example the triatomic quenching is found even for oxygen. This proves that efficient triplet state quenchers
need not necessarily have initially unpaired elec-
trons and the possibility of a mechanism different
from paramagnetic quenching, through which
diamagnetic quenchers operate, is evident.

Previous workers have shown that potassium
iodide and iodine are very effective quenchers for
triplet state. It is most unlikely that this is due
to enhancement of spin orbit interaction by the
heavy-atom effect of the dilute solvated iodide

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FIXED-BED STUDIES OF THE CATALYTIC DECOMPOSITION OF OZONE

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(Received April 1, 1969; revised July 15, 1969)

Results are reported of the catalytic decomposition of ozone, using metal oxide catalysts, in a fixed-bed reactor. These results are then discussed in the light of other work on similar studies given in the literature.

Introduction

Catalytic decomposition of ozone, using metal oxides, has been extensively made use of by research workers to study the reaction kinetics in aggregatively fluidised bed reactors. This reaction has certain unique characteristics making it suitable for such studies, namely, the strong absorption spectrum of ozone at a wavelength of 2537 Å, leading to easy and continuous measurements of ozone concentrations using spectrophotometric techniques, the wide choice of a catalyst, and the relative ease with which ozone can be generated from air or oxygen.

Since most studies of reaction kinetics in gas-solid fluidised bed reactors are carried out in parallel with fixed bed reactors, catalytic decomposition of ozone was studied in a fixed-bed reactor. The results of these studies are presented in this contribution along with their analysis, to ascertain the effect of various operating conditions on the rate of ozone decomposition.

Equipment

The fixed-bed reactor used was made of Pyrex glass and was about 1 in i.d. and 3 in long, having a sintered glass disc inside it to act as the catalyst support. The catalyst temperature was measured by a thermometer contained in a thin glass thermowell which extended from the top of the reactor to within a few millimeters of the sintered support. The reactor was contained in a liquid paraffin constant temperature bath, heated by a 250W immersion heater and provided with a mechanical stirrer to ensure a uniform temperature. A thermistor probe in a thin glass sheath was immersed in the oil bath and controlled the temperature to within half a degree over the range of 25°C to 140°C.

The inlet gas stream to the fixed bed was preheated in a helical glass coil in the thermostat which surrounded the reactor and was then made to flow downwards through the reactor. The gas flow to the reactor was controlled by a needle valve. A down flow of gas ensured a uniform gas distribution, avoiding any channelling or spouting. The gas flow rate was measured by a rotameter flowmeter and the inlet and outlet gas pressures were measured by two diaphragm pressure gauges. Inlet and outlet gas sample lines were connected to the ozone measuring equipment. The gas inlet line to the reactor was a 3/16-in dia copper tubing, all other gas lines being 3/16-in dia polyethylene or translucent elastic P.V.C. The fixed-bed reactor is shown in Fig. 1.

Ozone was obtained from a small scale laboratory type ozone generator supplied by E.C.D. Ltd. (U.K.). Dry oxygen from a cylinder was used for ozone generation, the use of air being avoided for this purpose because of the possibilities of the formation of oxides of nitrogen which can poison the catalyst. The ozone was diluted to a maximum of about 300 ppm by mixing it with a stream of dry air, obtained from the laboratory high pressure line through a pressure regulator valve. The air was dried through a calcium chloride
DILUTE SOLUTION PROPERTIES OF BISPHENOL A POLYCARBONATE: EXCLUDED VOLUME TREATMENTS

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The volume effects of bisphenol A polycarbonate in dilute solutions show a serious departure from Flory's theory. However, the variation of the swelling factor $\alpha$ with molecular weight conforms to the treatments of Kurata et al. and Fixman. Molecular weights below 20,000 do not seem to apply to any of the theories, probably indicating the limit of the excluded volume treatments.

Effects of excluded volume arising from interactions of nonbounded segments of polymer chains in dilute solutions is expressed in terms of the swelling factor $\alpha$. The swelling factor $\alpha$ is a function of a single variable $z$ defined by

$$z = B\left(\frac{\bar{R}^2}{M}\right)^{3/2}M$$  \hspace{1cm} (1)

where $B$ represents the polymer–solvent interaction parameter, $\bar{R}^2$ is the mean square radius of gyration in the unperturbed state and $M$, the molecular weight. The hydrodynamic treatment of Flory is

$$\alpha^3 - z = Cz.$$  \hspace{1cm} (2)

$C$ being a numerical constant. The ratio $(\alpha^3 - z)/M^3$ instead of being a constant increases with increasing molecular weight.\(^\text{2}\) Sitaramaiah\(^\text{3}\) also obtained a similar deviation for polycarbonate molecular weight. The hydrodynamic treatment of Flory\(^\text{1}\) is

$$\alpha^3 - z = Cz.$$  \hspace{1cm} (2)

$C$ being a numerical constant. The ratio $(\alpha^3 - z)/M^3$ instead of being a constant increases with increasing molecular weight.\(^\text{2}\) Sitaramaiah\(^\text{3}\) also obtained a similar deviation for polycarbonate solutions.

A number of statistical theories of excluded volume effects have been proposed by several authors.\(^\text{4}\)-\(^\text{6}\) These treatments are known as the third power law equations because of the term $\alpha^3$. Kurata et al.'s\(^\text{4}\) relationship is

$$\alpha^3 - z = \left(\frac{4}{3}\right)g(\alpha)z.$$  \hspace{1cm} (3)

where $g(\alpha) = \left[1 + \left(\frac{1}{3\alpha^2}\right)ight]^{-3/2}$  \hspace{1cm} (4)

Fixman\(^\text{5}\) has expressed the relationship in a simpler form,

$$\alpha^3 = 1 - 2z.$$  \hspace{1cm} (5)

Ptitsyn\(^\text{6}\) has recently proposed the following equation,

$$4.68\alpha^2 - 3.68)^{3/2} = 1 + 9.36z$$  \hspace{1cm} (6)

These equations are in good agreement with experimental data\(^\text{7,8}\) and with Monte Carlo calculations\(^\text{9,10}\) as well. Sitaramaiah\(^\text{3}\) also found that the behaviour of polycarbonate solutions fits in excellently with the treatment of Kurata et al.\(^\text{4}\)

**Experimental**

Determinations of viscosities and osmotic pressures at $25^\circ$C for polycarbonate fractions in different solvents have already been described.\(^\text{11,12}\) Molecular weights below 25,000 have been determined by vapour pressure osmometry at $37^\circ$C in chloroform.\(^\text{13}\)

**Results**

Values of the swelling factor $\alpha$ have been calculated from the relationships\(^\text{14,14a}\) between the intrinsic viscosity $[\eta]$ and molecular weight $M$,

$$[\eta] = K M^{1/2} \alpha^3$$  \hspace{1cm} (7)

$$[\eta] = K M^{1/2} + 0.51 B \Phi M.$$  \hspace{1cm} (8)

where $K = \Phi(6 \bar{R}^2/M)^{3/2}$  \hspace{1cm} (9)

$\Phi$ is the so-called universal constant and $\alpha \eta$ is the swelling factor determined from viscometric studies. $K$ values for different polycarbonate–solvent systems have been determined graphically\(^\text{15}\) using equation 8. Values of $\alpha \eta$ thus obtained are given in Table 1. Number average molecular weights $M_a$ are used in these calculations.

Figure 1 gives the plots of different theories for polycarbonate solutions in chloroform at $25^\circ$C. These plots have been drawn assuming the condition\(^\text{14}\) of equality between $\alpha$ and $\alpha \eta$.

**Discussion**

Figure 1 shows that Flory's relationship does not hold for polycarbonate solutions. The plot of $(\alpha^3 - \alpha^3)$ against $M_a$ makes an intercept on the abscissa as reported by Sitaramaiah.\(^\text{3}\) The plot of Ptitsyn's equation also gives a similar intercept and the modification suggested by Ueda and Kajitani\(^\text{6}\) does not indicate any improvement.
DETERMINATION OF MOLECULAR WEIGHT OF POLYMER WITH LOW DEGREE OF POLYMERIZATION

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Molecular weights of polycarbonate fractions in the range 5,000 to 22,000 have been determined by vapour pressure osmometer. The results are within 5% of the viscosity average molecular weights. Moreover, agreement between the molecular weights calculated from Raoult's law and from the Flory-Huggins treatment is of the same order. The polymer-solvent interaction parameter is somewhat higher, probably indicating the concentration dependence.

It is not possible to determine polymer molecular weights less than 25,000 either by osmometry or by light scattering method. Polymer molecules in this range of molecular weights are permeable to osmometer membrane and small amount of impurities cause much greater interference to the scattered light. Of the other methods, vapour pressure osmometer is convenient. It is, in fact, a vapour pressure lowering method in which the sensitivity is increased manifold by thermoelectric appliances. Vapour pressure lowering in polymer solutions is very small, of the order of $4 \times 10^{-3}$ mm of Hg. Measurements of such small differences require a very sensitive appliance.

Vapour pressure osmometer offers an indirect method of determining vapour pressure lowering. This thermoelectric osmometer based on the apparatus described by Hill and Baldes measures the steady state of temperature difference arising from different rates of solvent evaporation from solvent and solution. The temperature difference is assumed to be proportional to the difference in the vapour pressure which, in turn, is related to the molecular weight of the solute. The use of thermistors enables detection of a very small temperature difference and rapid attainment of equilibrium. The theory of the method has been discussed by Tomlinson et al. and van Dam.

Raoult’s law and the Flory-Huggins treatment are the theoretical basis of molecular weight determination by this method. The vapour pressure lowering due to a solute, according to Raoult’s law, is expressed by,

$$\left( p_2/p_0 \right) = \left( W_1/M_1 \right) / \left( W_1/M_1 + W_2/M_2 \right)$$  \hspace{1cm} (1)

where $p_0$ and $p_2$ are vapour pressures of solvent above solvent and solution respectively and $W$ and $M$ refer to weight and molecular weight with subscripts 1 and 2 denoting solvent and polymer. However, Raoult’s law does not hold even for dilute polymer solutions but equation 1 can be used to obtain apparent molecular weights for different concentrations, the extrapolation of which to zero concentration gives the true molecular weight.

The Flory-Huggins treatment is,

$$\left[ \ln \left( p_1/p_0 \right) - \ln \phi_1 \right] \phi_2 - 1 = -V_1/V_2 + \chi \phi_2$$  \hspace{1cm} (2)

where $\phi$ is the volume fraction, $V$ the molar volume, subscripts 1 and 2 referring to solvent and polymer respectively and $\chi$ is the polymer-solvent interaction parameter. A plot of the left hand side of equation 2 against $\phi_2$ should be rectilinear with an intercept $(-V_1/V_2)$ and a slope $\chi$. The molecular weight can be calculated from the intercept.

Experimental and Results

The apparatus and its operation have been described elsewhere. This is not an absolute method and the instrument must first be calibrated using a pure substance of known molecular weight in the solvent to be used in the determination of polymer molecular weight. Recrystallized benzil was used in chloroform with molar concentrations $m$ in the range 0.001 to 0.066 for calibration. The lowering of vapour pressure is read as a difference in resistance $\Delta R$ in ohms. The values of $\Delta R$ obtained are plotted against $m$ to get the calibration curve for the solvent (Fig. 1).

Fractionation of bisphenol A polycarbonate (makronol 3,000) has been described in previous papers. Values of $\Delta R$ for polycarbonate solutions in chloroform in the concentration range 0.5 to 1.75 g/dl were obtained. The experiment was carried out at 37°C and in all cases equilibrium values of $\Delta R$ were taken. For benzil solutions...
INFLUENCE OF ETHYLENE GLYCOL CONCENTRATION ON THE ACTIVATION ENERGY TRANSITIONS OF LIQUID WATER

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The study of concentration dependence of the jumps in $E_\eta$ for a number of aqueous solutions from 0% to 9.8% ethylene glycol is undertaken at increments of nearly 2% glycol. $E_\eta$ is obtained by using the Andrade equation after differentiation, viz.

$$E_\eta/R = \Delta \ln \eta / \Delta (1/T) = T^2 \Delta \ln \eta / \Delta T$$

For examining the course of the movements of the activation energy jumps as a function of concentration a chart is prepared for the various energy jumps. It is found that the shifts of these jumps with the change in concentration are mostly smooth, except, the region between 16°C to 30°C, where there is appearance and disappearance of certain steps with the change in magnitude of the jump.

Introduction

The previous measurements on flow activation energy, derivatives of dilatation and refractive index have shown the existence of discontinuities or anomalies, probably associated with the presence of structural transitions of some kind in the case of number of pure liquids and aqueous solutions. In the case of water–ethanol system, the discontinuities are found to be the functions of both temperature and concentration of solute. It has also been observed that the transition of these discontinuities are mostly uniform in character, but does not always follow the uniformity in some regions, where there is appearance and disappearance of certain steps with the changes in magnitude of the jump. Now, in order to clear up this point and to obtain further information on the character of structural transitions of liquid water associated with these discontinuities, another aqueous system such as water–ethylene glycol has been taken up for study. Some accurate work has already been done on the flow activation energy of pure ethylene glycol. The present communication describes similar measurements with dilute aqueous ethylene glycol solutions, covering the concentration range of 0% to 10% ethylene glycol (by weight) at intervals of about 2%.

Experimental Technique

The experimental technique is essentially the same as described for dilute alcohol by Ahsanullah and Qurashi. The activation energy of viscous flow ($E_\eta$) is measured with small temperature intervals $\Delta T = 1^\circ C$, by use of the differential method which is based on the differential of the Andrade equation, viz.

$$E_\eta / R = \Delta \ln \eta / \Delta (1/T) = -T^2 \Delta \ln \eta / \Delta T$$

where $\rho$ is the density, $\nu$ the kinematic viscosity, $\eta$ the dynamic viscosity ($= \eta \times \rho$) and $\beta$ is the coefficient of dilatation (the term $T^2 \beta$ forms a small slowly varying correction factor which can be applied to the final $E_\eta / R$ values). An analysis of basic differential technique has been made (Ahsanullah) and found fully adequate for the study of small scale variation in $E_\eta$.

The time of flow are measured by a U-tube viscometer no. 1 of B.S.S. pattern to an accuracy of $\pm 0.02$ sec with a calibrated stop-watch. Townson and Mercer thermostat is used in which Beckmann differential thermometer never showed a variation of more than $0.002^\circ C$ in the temperature range studied. Correction for the change of equilibrium level of the liquid in the viscometer is usually applied, and the evaporation losses at high temperature (above $35^\circ C$) are diminished by keeping a ballast bottle device well immersed in the thermostat as fully described by Qurashi and Ahsanullah. The errors due to variation of viscometer constants with temperature due to thermal expansion of viscometer and variation of precise magnitude of the differential Beckmann thermomter scale due to expulsion of the excess mercury at each resetting after $5^\circ C$, are also considered.

Measurements on 4.5% and 9.8% Ethylene Glycol in Water by Weight

The water–ethylene glycol solutions are prepared by adding a calculated quantity of pure redistilled glycol to thrice distilled water in a stoppered flask and shaking thoroughly. The glycol percentages are then checked by the measurement of density, and also by viscosity measurement at a suitable temperature during the main experiment. The first series of measurements are carried out with 4.5% and 9.8% solutions (by weight) which have viscosity nearly 2% and 4% higher than water.
SOLVENT-EFFECTS IN THE EPOXIDATION OF CYCLOHEXENE

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Epoxidation of cyclohexene with peroxy and \( p \)-substituted peroxybenzoic acids has been studied kinetically in methanol at 30°, 40°, and 50°C(±0.5°) and with peroxybenzoic acid in ethanol, acetone and n-propanol at 40°C(±0.5°). A \( p \) value of +1.30 has been calculated by the Hammett treatment. Energies of activation, entropies of activation and frequency factors have also been calculated. The differences in rate constants have not been found to be significantly dependent either on differences in energies or entropies of activation. However, the rate constants have been observed to be inversely proportional to the dielectric constants of the solvents employed. The addition of corresponding non-peroxybenzoic acids has been shown to cause no catalytic effects on the rate of this reaction.

Oxidation of cyclohexene to afford an epoxide has been known for a long time now.1 This general reaction of the cyclic olefin with different oxidants has been the subject of various investigations.2–7 However, Medvedev and Blokh8 first reported the kinetics of the oxidation of cyclohexene using \( p \)-methoxy- and \( p \)-nitroperoxybenzoic acid in benzene and xylene. They found that in these aprotic solvents the oxidation is a bimolecular process. From these studies, the authors worked out various kinetic parameters and calculated a \( p \) value of +0.94. Later, Stuurman9 studied this oxidation with peracetic acid and also showed that this is a bimolecular reaction.

In connection with another study, it was desired to know the behaviour of polar solvents when olefins were oxidised with \( p \)-substituted peroxybenzoic acids. Since Medvedev and Blokh had determined the \( p \) value of this oxidation by using only two \( p \)-substituted peroxybenzoic acids, we decided to extend this work in polar solvents to employ more than two substituted peroxybenzoic acids. Thus, the present study describes the effects of polar solvents in the oxidation of cyclohexene with peroxy- and \( p \)-substituted peroxybenzoic acids (\( p \)-RC\(_6\)H\(_4\)O\(_3\)H where \( R = \text{NO}_2\), Cl, CH\(_3\) and OCH\(_3\)).

Results and Discussion

The rate constants for the oxidation of cyclohexene with peroxy- and four \( p \)-substituted peroxybenzoic acids were determined in methanol at 30°, 40° and 50°C (±0.5°) and with peroxybenzoic acid in ethanol, acetone and n-propanol at 40°C (±0.5°). In all these cases strict adherence to second order kinetics was noted. The rate constants obtained with varying concentration of cyclohexene and unsubstituted/\( p \)-substituted peroxybenzoic acids in the presence of corresponding acids, also, followed the same order of the reaction. The activation energies and physical factors were calculated from the Arrhenius plots shown in Fig. 1. The entropy of activation, \( \Delta S^\ddagger \), was determined from frequency factors.10 “A”. The various physical constants as obtained in these studies are given in Table 1. It is obvious from the plot of \( E \) versus \( T \Delta S^\ddagger \), depicted in Fig. 2, that there is a linear increase of \( \Delta S^\ddagger \) with increasing activation energies. Generally the rate constants show their dependency on the difference of both energies and entropies of activation.11–12 However, in the present studies there appears no regular trend as regards this dependency.

Effect of Acids.—The addition of corresponding benzoic acids in the systems concerned did not show any catalytic effect on the rate of reaction. As a result of the addition of these acids only slight differences in rate constants were observed which fall within the limits of experimental errors (Tables 1 and 2). This confirms that respective acids, formed as products, do not catalyse the reaction.

Solvent Effect.—The nature of the solvent, generally affects the rate of reaction. In order to investigate this aspect, the epoxidation of cyclohexene with peroxybenzoic acid was carried out in methanol, ethanol, acetone and n-propanol (arranged in the ascending order of their dielectric constants).13 The rate constants obtained in these solvents at 40°C±0.5° along with their dielectric constants are recorded in Table 2. A plot of rate constants versus the reciprocal of dielectric constants of the solvents employed gives a straight line as shown in Fig. 3. It is, therefore, apparent that the rate constants are inversely proportional.
THE BASIC STRENGTH OF 2-METHYL INDOLE

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The best possible $pK_a$ value of 2-methyl indole is found spectrophotometrically using the Hammett's $H_0$ indicator method. The value comes out to be $-0.19$. The problem of polymerization of 2-methyl indole in high concentration of acid solutions has been overcome by extrapolation method and differential plot.

Indole, furan, pyrrole and thiophene form a distinct group of aromatic heterocyclic compounds in which there is enhanced sharing of the electrons on the four carbon atoms by comparison with the sharing in six-membered compounds such as pyridine. Albert describes the former as $\pi$-excessive and the later as $\pi$-deficient. Longuet-Higgins and Coulson estimated on theoretical grounds that heterocyclic compounds should be very weakly basic, although their basicity has not been determined until recently. For the estimation of the $pK_a$ value of a very weak base, special methods are necessary, for which the Hammett indicator method, employing a spectrophotometric technique, is versatile and satisfactory.

The basic strength of 2-methyl indole has been studied by Bertl et al. and by Hinman and Lang, who have obtained values $-0.10$ and $-0.28$, respectively. They used the same technique for $pK_a$ determination, but overlooked the ready resinification of these compounds in strongly acid media as pointed out earlier by Fernando and Naqvi. Fernando and Naqvi overcame this problem by studying the kinetics of the resinification of pyrrole and thus obtained extrapolated values of acid absorption at zero time. A similar method has been employed in the present work to obtain an accurate $pK_a$ value for 2-methyl indole.

**Experimental**

*Material.*—The compound 2-methyl indole of L. Light & Co. Ltd. that was available in sufficiently pure form was used. m.p. 59°C, b.p. 270°C. Methanol and cyclohexane of B.D.H. Ltd. of analytical grade were further purified, the former by redistillation and the latter by adsorption chromatographic technique. H$_2$SO$_4$ of E. Merck Co. Ltd. used was of 98.98% purity.

*Preparation of Solutions.*—Stock solutions of 2-methyl indole ($10^{-3}$ M, $10^{-4}$ M), were prepared in methanol.

A stock solution of 5M H$_2$SO$_4$ was prepared and from it 0.20, 0.30, 0.40, 0.50 and a range from 1.2 to 3.66 molar acid were prepared in doubly distilled water.

10 ml of 2-methyl indole ($10^{-4}$M) was added to different solutions of H$_2$SO$_4$ and made up to 100 ml. Thus a $10^{-3}$M was prepared in sulphuric acid of different concentration. Also prepared 4.5, 6, 7, 8, 9 x $10^{-4}$ and 10 x $10^{-3}$ molar solutions from $10^{-4}$M 2-methyl indole.

**Procedure.**—All studies made in this work were performed on Hilger's ultraviolet and visible spectrophotometer, Model H-108. For checking the performance of instrument absorption of two standard compounds, namely potassium chromate and potassium nitrate were studied. Absorption maxima of potassium chromate and potassium nitrate were found at 273 and 920 nm and are in good agreement with the standard.

**Ultraviolet Spectra of 2-Methyl Indole in H$_2$SO$_4$ Solutions.**—$10^{-5}$M 2-methyl indole solutions in H$_2$SO$_4$ (0.2 to 0.5M) were run in ultraviolet and the absorbancies were noted (Fig. 1).

The absorption spectra of 2-methyl indole ($4.6, 8 \times 10^{-4}$ and $10^{-5}$M) in methanol were taken at different wavelengths. The absorbancies are shown in Fig. 2.

**Spectrophotometric determination of $pK_a$ of 2-Methyl Indole.**—From the stock solution of 2-methyl indole ($10^{-4}$M) 10 ml of the solution was sucked and added to a 100-ml flask containing 90 ml standard H$_2$SO$_4$, ranging from 1.2 to 3.66 molar acid. The absorbancies were taken with respect to time and stopwatch was started at the half delivery of 10$^{-4}$M 2-methyl indole solution from pipette. The solution was at once shaken and the absorbancies were noted at 273 nm in silica cell. The absorption curves were obtained for each solution and the values extrapolated to zero time (Table 1).
CHEMICAL INVESTIGATION OF ANTICHRIS LINEARIS HOCHST. PART I

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From Anticharis linearis Hochst, two hydroxy lactones $C_{11}H_{16}O_5$, m.p. 123-24°C, $C_{17}H_{26}O_{10}$, m.p. 182-83°C, provisionally named as linearin and linearoside, respectively, have been isolated. A crystalline polyhydroxy compound and an aliphatic hydrocarbon identified as mannitol and triaccontane, respectively, have also been isolated.

The plant Anticharis linearis Hochst (Scrophulari-aceae) grows on the hills of Thanabulakhan (District Dadu) and is also found scattered in the Plains of Jamshoro and Khairpur in the province of Sind. It is used by the locals as a cure for diabetes mellitus. The plant is an annual herb with linear leaves and violet flowers flourishing in the month of September-October and not exceeding a maximum height of six inches to 1 ft. It is usually available after summer rainfall.

It will be interesting to note that a number of members of Scrophulariaceae family have been reported in indigenous medicine to be useful in the treatment of diabetes. Chemical examination of the above plant was undertaken to correlate the results with the investigations on the other two members of the same family being simultaneously carried out in these laboratories.

Preliminary pharmacological studies of the above plant revealed that when water extract of the semidried plant was injected into rats and dogs, marked variations in blood pressure were observed and in few cases stimulation of heart was also noticed. On the other hand, preliminary chemical examination revealed that the plant is fairly rich as far as the glycosides are concerned. Some other active principles have also been isolated. Many members of this family have been found to contain glycosides. R. Jaretzky and H. Ulrici investigated about sixty species of the family and identified cardioactive glucosides in many members.

The scheme for the isolation of the compounds is given in the chart.

Linearin was obtained from the watersoluble portion of the chloroform fraction, on passing through a column of alumina with benzene as the solvent. It reduced dilute potassium permanganate solution and decolourised bromine in acetic acid. It had m.p. 123-24°C and analysed for $C_{11}H_{16}O_5$. Its IR spectrum (Fig. 1) revealed the presence of unsaturation hydroxy and keto groups. No derivative of keto group could be prepared. The UV light absorption, however, was typical of $\alpha,\beta$-unsaturated carboxyl group. It gives positive hydroxamic acid test indicating a lactonic or ester function and liberates carbon dioxide on hydrolysis with dil. $H_2SO_4$. These tests show the presence of lactone group. The main peaks in IR and UV were comparable with those of $\beta$-hydroxy butenolides (tetronic acids) which are also known to shed off carbon dioxide on hydrolysis with dilute acids.

The ethyl acetate fraction, on purification by passing through a column of alumina with ethyl acetate as the eluent, gave needles of linearoside which melted at 182-83°C. It analysed for $C_{17}H_{26}O_{10}$ and showed peaks of keto unsaturation and hydroxy groups in the IR region (Fig. 2). It formed a crystalline tetracetate, m.p. 196-38°C and tetrabenzoate, m.p. 156-58°C. It evolved carbon dioxide on heating at 250-80°C and the residue crystallised from benzene m.p. 165-68°C. It showed no carbonyl absorption in the IR spectrum. On chromic acid oxidation linearin was obtained which shows that linearoside is structurally related to linearin.

The ethyl alcohol fraction on concentration and cooling gave white needles, m.p. 163-64°C. Its IR spectrum was superimposable on that of $D$-mannitol. Its mixed m.p. with an authentic sample and mixed m.p. (123-25°C) of its acetate with that of $D$-mannitol acetate confirmed it as $D$-mannitol.

Besides mannitol, glucose and mannose were present in the alcohol fraction when examined by paper chromatography. $D$-Glucose and $D$-mannose were also isolated as phenyl hydrazone derivatives.

Two more hydroxy compounds named as anticharol, m.p. 296-98°C and linearol, b.p. 148-49°C/0.2 mm, have been isolated from the water-insoluble residue of the alcoholic extract. Their acetate derivatives, anticharol acetate, m.p.
A NEW TECHNIQUE FOR THE STUDY OF COPPER-ACETAMIDE SYSTEM IN AQUEOUS SOLUTION

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The new technique called "continuous variation method", proved to be as reliable as the conventional monovariation method. The complex in the ratios 1:2 and 1:4 were observed. A reasonable structure for the complex is also suggested.

A monovariation method is usually employed to study the interactions of metals with organic compounds in aqueous solution. But the study of complex formation by this method involves the preparation of a very large number of specimens and the standardization of instrument for each experiment. To avoid such tedious and time consuming experiments, a new technique, called "continuous variation method" has been adopted. In this, a small volume of concentrated metal solution is added in steps to a known volume of comparable dilute solution of ligand-forming compound to study the changes in the physical properties of the system. Physical properties like density, viscosity, surface tension and refractive index are studied. The results obtained by this method were verified by the conventional monovariation method.

Results and Discussion

The plots in Fig. 1 and 2 show two kinks at 0.25 and 0.5 CuSO4/acetamide ratio, respectively. The refractive index composition curve in Fig. 3 shows only one kink at 0.5 ratio. The kink at 0.25 could not be detected because the change in refractive index with the change of components concentration is relatively small at lower concentrations and is not easily detectable with the instrument used.

The density, viscosity and surface changes measured by monovariation method are shown in Fig. 4, 5 and 6. The results are in agreement with the plots shown in Figs. 1, 2 and 3 showing the reliability of our techniques. The sharp changes in physical properties at 0.25 and 0.5 show additive complexing of copper sulphate and acetamide molecule.

The coordination number of copper is four and it has nine electrons in the d level which may lead to formation of a square planner complex. In the present case, copper ion receives electron from nitrogen and the sharing of electrons pair through vacant orbitals of copper(II) ions will lead to partial covalent nature of metal-ligand bond. If it is assumed that the two aceta-
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PHYSICAL SCIENCES SECTION


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THE ALKALOIDS OF DELPHINIUM VESTITUM WALL: ISOLATION AND CHARACTERIZATION OF LYCOCTONINE

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SOME PRELIMINARY STUDIES OF THE PHARMACOLOGICAL ACTIVITIES OF SCHinus MOLLE LINN

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Aqueous extracts of the fruit, leaf and stem of the Californian pepper tree (Schinus molle) were pharmacologically active. Extracts prepared from the fruit were the most active. All the extracts caused a direct depression of myocardium and dilatation of blood vessels resulting in a fall in blood pressure. The smooth muscles of rabbit and guinea pig intestine were depressed after an initial stimulation. The action seems to be a direct one but in the anaesthetized dog central vagal stimulation was found to be an additional factor. The non-gravid uterus of rat and rabbit was not affected but gravid uterus was greatly stimulated. Musis was observed both on local and systemic administration of the extracts. Smaller doses had no effect on the central nervous system; higher doses produced anaesthesia and paresis of the muscles of extremities. Fatal doses produced convulsions and the animals died from respiratory failure. All the extracts were saponin-free. However, the possibility of the presence of essential oils, though only in traces, producing some or all of these actions, cannot be ruled out at the present stage.

Schinus molle L., the Californian pepper tree, is cultivated as an ornamental tree in certain areas of the northern part of West Pakistan and of Azad Kashmir. It belongs to the family Anacardiaceae and is evergreen, attaining a height of about 20 feet. Its botanical description has been given by Parker. On a preliminary screening, various parts of the plant were found to be pharmacologically active. The authors could not find any published information on its pharmacological or medicinal properties. Hence a pharmacological study of the plant was indicated. The present work deals with such a study on the fruit, leaf and stem of the plant.

Materials

Preparation of Extracts.—Two different procedures were employed to prepare aqueous extracts.

Aqueous Extract (I).—Crushed or powdered material (100 g) was soaked in distilled water for 24 hr. The menstrum was passed through a muslin cloth and the filtrate was then centrifuged at 4000–5000 rev/min for 20–30 min. The supernatant was filtered through ordinary filter paper and its volume was adjusted to 100 ml with distilled water.

Aqueous Extract (II).—Crushed material (100 g) was soaked in commercial ethanol (95%) for 24 hr. The menstrum was first passed through a muslin cloth and then through ordinary filter paper. The filtrate was concentrated to a semi-solid mass under reduced pressure at 40 to 50°C. The residue was treated with 50–70 ml chloroform and transferred to a separating funnel to remove chlorophyll. 15 ml distilled water was added to the funnel and, after shaking, was allowed to stand for about 30 min to settle. The upper aqueous fraction was removed and the lower chloroform fraction was again treated in a similar manner with 15 ml distilled water. The procedure was repeated 4 times. The aqueous fractions were added, heated on a water bath until the smell of chloroform had disappeared and filtered. The filtrate was neutralized to pH 6.8 (checked with an electric pH meter) with dilute ammonia solution and was made up to 100 ml with distilled water. The pH was not brought to 7.0, as when doing so sometimes a turbidity was observed.

Removal of Saponins.—Saponins were removed by a method mentioned by Peach and Tracy by treating the extract with about 6 g charcoal, boiling it on a water bath and filtering it. The procedure was repeated thrice or more until saponins were completely removed. All such extracts when taken up with water neither gave a froth on shaking nor haemolysed mammalian red blood corpuscles.

Potassium estimations of the extracts were done with a flame photometer.

One ml of the extracts represents 1 g of the crude material.
PHARMACOLOGICAL ACTIVITY OF AN ALKALOID FROM SARCOCCOA SALIGNA

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A shining crystalline base, isolated from the leaves of Sarcoccoa saligna Muel (Fam. Euphorbiaceae) was tested for its biological activity. The effect of the drug on neuromuscular transmission in the mammalian skeletal muscle was found to be remarkable. At low concentrations, it potentiated the action of naturally secreted acetylcholine in the isolated rat diaphragm, stimulated via the phrenic nerve. The drug was also found to possess local anaesthetic property when it was administered intradermally into the guinea-pig skin. Its acute toxicity in the intact animal and its effects on other systems of the body were also studied. The results of the biological investigations are described and the possible mode of action of the drug is discussed.

Sarcoccoa saligna Muel (Fam. Euphorbiaceae) is an evergreen shrub found sparsely distributed throughout the northern region of West Pakistan. A shining crystalline base, m.p. 229-30°C, was isolated by Kiamuddin and Haque1 from its leaves. Its molecular formula was determined as C29H52N2O and specific rotation as [α]D + 18.5 in MeOH. The compound appeared to be a tertiary base. Since the plant itself was reported to be used by the local people as a useful drug, the work on the biological activity of its alkaloid seemed to be of some interest. The water-soluble tartrate of the alkaloid was used in various biological tests but the doses shown in this text represent the free base.

Experimental

Acute Toxicity

A dose of 100 mg/kg in the mice, given subcutaneously was lethal in a group of 6 animals. The toxic symptoms consisted of excitement, tremor, ataxia, hyperpnoea followed by hypopnoea, hypertonia and eventual convulsions leading to death. The pupils were moderately constricted at the time of death. Symptoms started about 10 min after injections and the animals died within an hour. On post mortem examination, no sign of local irritation or vascular changes could be detected at the site of injection. The lungs were found to be pale and collapsed. No pathological changes could be detected in any of the internal organs. Another group of 6 animals survived a dose of 40 mg/kg.

Cardiovascular and Respiratory Effects

The effects of the drug on blood pressure, heart-rate and respiration have been studied in anaesthetised rat and cat. In the rat under urethane anaesthesia, 10 mg/kg of the alkaloid given by intravenous infusion produced a marked but temporary fall of the blood pressure which lasted for 5-10 min. There was a transient slowing of the heart immediately after the injection. The pressure response to nicotine was much reduced but the responses to adrenaline, noradrenaline, acetylcholine and carotid occlusion for 30 sec were not affected in the period immediately after the injection of the alkaloid. The hypotensive effect of the test material was not antagonised by atropine or mepyramine but after atropine the animal could stand a larger dose of the alkaloid, which would otherwise have been lethal. The effects produced by stimulation of the peripheral end of the cut vagus nerve were reduced after a single dose of 10 mg/kg of the alkaloid. After a total of 30 mg/kg of the alkaloid given in three divided doses, the effect of vagal stimulation was totally abolished and returned only gradually after an hour.

In the cat under chloralose anaesthesia, a dose of 20 mg/kg produced a temporary fall of blood pressure lasting for 2-5 min. The alkaloid produced irregularity in respiratory rate and rhythm, which could be relieved by atropine. In this species also it was observed that the anaesthetised animals could stand larger doses of the alkaloid after atropine than what would have been lethal without atropine.

Effect on Isolated Rabbit Heart

The effect of the alkaloid was studied in the isolated rabbit heart perfused by Langendorff's technique. On this preparation 0.1 mg alkaloid produced bradycardia accompanied by a decrease in the force of cardiac contractions. The heart, however, could recover from this dose. But when the dose was increased to 1.0 mg, the depression of the heart increased and it stopped ultimately.

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BIOCHEMICAL AND QUALITY CHANGES IN POST-RIGOR OVINE MUSCLE AFTER THAWING AT LOW AND HIGH TEMPERATURE

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A study was made of the effects of freezing followed by thawing at low (8°C) and high (25°C) temperature upon some physical and chemical properties of the post-rigor ovine longissimus dorsi muscle. Measurements of total nitrogen, protein nitrogen (PN), non-protein nitrogen (NPN), acidic and basic groups, moisture content, pH value, refractive index and tenderness were made on the muscle and its exudate squeezed out under defined conditions. A new refractometric method for the determination of protein alterations has been evaluated.

Tenderness of the cooked meat was linearly related to PN, % PN/TN, and % NPN/PN of the muscle, but was not related to the refractive index of the muscle exudate.

The relation of various nitrogenous components of the exudate was plotted against tenderness. There was no relationship between ultimate pH value and moisture content of muscle or muscle exudate. Cooked meat tenderness increased with increase of acidic and basic groups on the muscle proteins and moisture content of the muscle up to a certain level and thereafter the trend was reversed. Possible explanations for various changes in muscle components after freezing and thawing and their relation with tenderness have been discussed.

Following slaughter, a series of changes take place in the physical and chemical properties of muscle. Some are independent of outside agencies and others may be due to microorganisms on the surface or within the carcass of the animal, nearly all can be slowed down or almost checked by lowering the temperature of the tissue. Hence the changes affected in muscle tissue by chilling, freezing and thawing are of great economic importance.

Freezing alone has no demonstrable effect upon the colour, flavour, odour or juiciness of meat as judged after cooking but it does affect the raw muscular tissue due to the formation of hard ice crystals and the concentration of mineral constituents which gradually damage the proteins and irreversibly alter them.

When thawed the frozen meat has a tendency to exude a viscous reddish brown fluid known as drip, the quantity of which is affected by the method of thawing, as also is tenderness. The presence of drip and, to a lesser extent, the colour of the meat serve to identify frozen from unfrozen tissue.

Frozen meat cooked after thawing for 48 hours is slightly less tender than its chilled counterpart. Miller and May concluded that it is not the rate of freezing that significantly affects tenderness in chicken meat but the temperature of storage after freezing. Cook and Langsworth found that ovine longissimus dorsi muscle frozen pre-rigor and thawed for 24 hr at temperature up to 40°C was significantly more tender than unfrozen muscle. Furthermore, the meat thawed at 5°C was significantly more tender than meat thawed at 10, 15 or 20°C.

The refractometric properties of the components of meats have been used by a number of workers as indices of its characteristics. Thus, Weiribicki et al. used the refractive index of extracted proteins of beef as a measure of and as a guide to the tenderness of meat. For determination of anatomical differences in the fat of beef longissimus dorsi, Cook, Bray and Weckel made use of the refractometric properties of fat. The use of refractive index for the evaluation of protein denaturation in cod was suggested and used by Elerian. A similar photometric technique of cell fragility measurement was developed by Love and Mackay to estimate the extent of protein denaturation in cold stored cod muscle. No such technique has been used for measuring protein denaturation in ovine muscle exudate obtained by squeezing under defined conditions.

This study was undertaken to ascertain the effects of thawing ovine muscle, at low and high temperature, on changes in protein and some other quality characteristics. A new refractometric method was evaluated for the estimation of protein denaturation and its possible relation with meat tenderness.
A NEW SPECIES OF RHIZOGLYPHUS FROM PAKISTAN
(ACARINA : TYROGLYPHIDAE)

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(Received May 10, 1969)

A new species of Rhizoglyphus karachiensis, collected from the manure of dairy cattle in Karachi is described and illustrated.

Female (Figs. 1–6)

Dimensions.—Idiosomal length 1190 μ; width 812 μ (average of 8 specimens).

Dorsum.—Cuticle thin, smooth and colourless, body oval, dividing into propodosoma and hysterosoma. Two brown spots on either side of the body in the position of posterior lateral setae (lp). Propodosoma with a pair of internal vertical (vi) on anterior margin. External vertical (ve) lacking. External scapular (sce) three times as long as internal scapular (sci), sce being the longest body seta. On hysterosoma dorsal seta (d3) longer than d1, d2 and d4; d1 being the smallest. External humeral (he) twice as long as internal humeral (hi), vi and he longer than sci. External sacral (sac), internal humeral (hi) and dorsal seta (d4) relatively shorter than other setae on hysterosoma.

Fig. 1.—Rhizoglyphus karachiensis n. sp. (dorsum of female).

Fig. 2.—Rhizoglyphus karachiensis n. sp. (venter of female).
THE BRACHYURAN LARVAE OF WEST PAKISTAN HATCHED IN THE LABORATORY

Part III.—Portunidae: Thalamita (Decapoda: Crustacea)

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Three species of genus Thalamita have been hatched in the laboratory and early larval stages obtained, figured and described. Prezoea and first zoea of T. crenata (Milne-Edwards), T. prymna (Herbst), and first and second zoea of T. admeta (Herbst) are described.

Introduction

Out of 19 species of family Portunidae, recorded from Karachi, 11,2,3 three belonged to the genus Thalamita, which are dealt herewith. Only prezoea and first zoea of T. crenata (Milne-Edwards) have been described by Prasad and Tampi3 and criticized by Chhapgar.4 Description of the prezoea and first zoea of T. prymna (Herbst) and first and second zoea of T. admeta (Herbst) is new to science.

Lebour5 reared Portunus puber (L.) and many workers described larvae of Carcinus maenas (Penn.) in Britain; Churchill,6 Hopkins7,8 and Costlow, Rees and Bookhout9,10 described the larvae of Callinectes sapidus (Rathbun) in America; Aikawa 11,12,13 worked on the Genus Portunus and Charybdis; Arriola,14 on Scylla serrata; Yatsuzuke15 on Charybdis japonica; Prasad and Tampi3 on Neptunus pelagicus; Naidu16 on Neptunus sanguinolentus and Scylla serrata; Chhapgar4 N. sanguinolentus, N. pelagicus and Charybdis orientalis; and Sin17 on Scylla serrata but the genus Thalamita has so far been neglected.

Materials and Method

Ovigerous females of T. crenata, T. prymna and T. admeta were collected from Buleji rocks, Manora island, Break waters, West Wharf, and Korangi creek, Karachi during 1964–65.

Rearing methods were used as described by Costlow and Bookhout.10 Temperature and salinity were maintained at 30°C and 35 ppt respectively throughout the experiments.

Moulting Periods.—Eggs of T. crenata and T. prymna hatched into prezoea which moulted after 6–7 hr into the first zoea which could not survive longer than 3 days and died without moulting. Eggs of T. admeta hatched into first zoea and no prezoeal stage was found. First zoea hatched after 5 days into the second zoea which died after 2 days before moulting.

1. Thalamita crenata (Milne-Edwards)

Prezoea: It is 1937µ in total length; the dorsal spine is longer than the rostral spine of the cephalothorax (220 and 191µ respectively); rudimentary lateral spines (58µ) emerge on the cephalothorax.

Abdomen: Pair of lateral knobs of the second segment point outwards and of the third segment bent downwards; postero-lateral spines of three to five segments overlap the next; telson fork depth is slightly more than its body length (117 and 103µ respectively); one small and one large spine on the prong of the telson.

Antennule: is short (88µ) and bears two aesthetes and one seta.

Antenna: Protopodite (191µ) is as long as the rostral spine of the cephalothorax; bears small teeth; exopodite (58µ) bears two setae.

Mandible bears four large and several small teeth on dorsal and ventral side.

Maxillule bears six plumose setae on coxal endite; five setose spines on basal endite; six long plumose setae on terminal and one small seta on basal segment of the endopodite.

Maxilla bears four (2+2) plumose setae on coxal endites; six setae (3+3) on basal endites; two terminal and two sub-terminal setae on the endopodite; four thick plumose setae emerge on the margin of scaphognathite which terminates as a thick setose spine.

First maxilliped has no seta on the basis; four swimming setae emerge on the exopodite; five segmented endopodite has setation 3,2,1,2,4+1 respectively.

Second maxilliped has no seta on the basis; four swimming setae emerge on the exopodite; three segmented endopodite bears 1,1,5 setae respectively.
PETKOLIN, A NEW OVICIDE WITH A SUMMARY ON OVICIDES AND PETKOLINS

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(Received May 5, 1969; revised June 11, 1969)

A summary of the toxicology of Petkols and note on ovicides is given along with the finding that Petkolin A could be used as an ovicide against the mosquito, Aedes aegypti (L.).

The Petkols (Petkolin A; Petkolin M, Petkolin S and Petkolin) which are chlorinated hydrocarbon (petroleum oil) type of insecticides have proved effective pesticides against many arthropod pests in the laboratory as well as in the field, are comparatively safer for mammals and fish, and are also non-phytotoxic (Table 1).

Insect control requires striking the pest at the weakest link. Although the egg stage is most vulnerable in most cases it is the least studied one in the Arthropoda. We have studied in the laboratory the ovicidal properties of Petkolin A against the mosquito, Aedes aegypti. In this insect the eggs are exposed to the toxic action of the ovicide, are susceptible to it, and a sufficient portion of the population is exposed in the egg stage for treatment. Ovicides other than Petkolin are the dinitro compounds, petroleum oils, organophosphorous insecticides, chlorinated hydrocarbon and cyclodiene insecticides, carbamates, indop polybutenes and various acaricides (Table 1).

Material and Methods

The insect Aedes aegypti (L.) was reared in the insectary. Aedes aegypti eggs were taken from the insectary to test the ovicidal effect of Petkolin A. Different concentrations ranging from 0.005 to 0.05% of Petkolin A were prepared in water. A 2% stock solution of Petkolin A was prepared in acetone. From this stock solution further dilutions were prepared in 250 ml of water.

For dipping the eggs crystallizing dishes (size 10 × 5 cm) were used. Twenty five eggs of mosquito were dipped against each concentration of Petkolin A. Readings were taken after 24 hr. Each experiment was run in duplicate. All experiments were repeated ten times. Controls were also run for each experiment. The percent mortality was calculated by using Abbot's formula and LC 95 (0.013) value was calculated by probit analysis (Fig. 1).

Results

Results with various concentrations are given in Table 3.

As a result of present investigation it is concluded that Petkolin A can be used effectively for the control of mosquito eggs. The concentration 0.025% of Petkolin A is most effective as it gives 100% mortality in case of mosquito eggs. No delayed hatching was observed.

Table 1.—Toxicology of Petkolin.

<table>
<thead>
<tr>
<th>Tested against</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton aphid, <em>Aphis gossypii</em></td>
<td>Petkolin A, Petkolin M and Petkolin S were tried against aperous agamic female. Petkolin S was as effective as BHC and more toxic than Endrin</td>
<td>4</td>
</tr>
<tr>
<td>White rats using Petkolin M</td>
<td>Much less toxic than BHC and DDT</td>
<td>13</td>
</tr>
<tr>
<td>Crop Pests: <em>Pyrrilla</em>, <em>Begada pita</em>, <em>maize borers</em>, <em>cotton jassids</em>, <em>cotton mites</em>, <em>grasshoppers</em> (<em>Chortogonous sp.</em>), <em>Plutella</em> sp. (caterpillars), <em>cotton leaf rollers</em>, <em>cabbage butterfly</em>, <em>turnip</em> hairy caterpillar, <em>groundnut mites</em>, <em>potato jassids</em>, <em>wheat weevil</em>, <em>black ants</em>, <em>citrus leaf miner</em>, <em>date palm</em> scales, and <em>date palm gall insects</em></td>
<td>Effective field control. Not phytotoxic against: Wheat (<em>Triticum aestivum</em> L); maize (<em>Zea mays</em> L); sugar cane (<em>Saccharum officinarum</em> L); <em>cotton</em> (<em>Gossypium hirsutum</em> L); <em>tomato</em> (<em>Lycopersicum esculentum</em> Mill.); <em>cabbage</em> (<em>Brassica oleracea</em> L); <em>beet root</em> (<em>Beta vulgaris</em> L); <em>bean</em> (<em>Dolichos lablab</em> L); <em>mung bean</em> (<em>Phaseolus aureus</em> Roth.); <em>smooth gourd</em> (<em>Luffa aegyptiaca</em> Mill.); and <em>pumpkin</em> (<em>Cucurbita maxima</em> Duch.)</td>
<td>12, 9</td>
</tr>
<tr>
<td>Housefly, <em>Musca domestica</em> (L.)</td>
<td>The chlorinated fractions in the boiling range of 130–190°C were better insecticides than the lower boiling fractions</td>
<td>11</td>
</tr>
<tr>
<td>Albino rat</td>
<td>LD50 value for petkolin was 9000–1100 mg/kg by subcutaneous injection</td>
<td>9</td>
</tr>
<tr>
<td>Cockroach, <em>Periplaneta americana</em>; mosquito, <em>Aedes aegypti</em> larvae; and flies</td>
<td>Petkolin was more toxic than Makrolin against flies and mosquito larvae but less toxic against cockroaches</td>
<td>8.79, 80.5–10</td>
</tr>
</tbody>
</table>

*Present address: P.O. Box 266, Dammam, Saudi Arabia.
The red cotton bug, *Dysdercus Koenigi* (Fab.), is known to feed upon many different species of malaceous plants. In East Pakistan the okra plant, *Hibiscus esculentus* Linn., is one of the most favourite host plant and the bug often causes serious damage to its leaves and young pods. Manickavasagar* studied the control of this pest in Ceylon. In a field of okra he applied emulsion sprays of DDT, dieldrin, chlordane and BHC and obtained significant mortality with the first three insecticides. Trehan *et al.*, evaluated toxicity of several insecticides against the red cotton bug. He found gamma-BHC, endrin, parathion and aldrin quite toxic to this insect.

Several methods of applying systemic insecticides have been reported, however, application of toxicants to stem is comparatively a new approach to the pesticide research. A number of workers have demonstrated that application of systemic insecticides to the basal part of the main stem of plants is an effective method of controlling certain pests. Linquist *et al.* stated that stem treatment provides a much more efficient method of applying certain systemic insecticides to cotton than seed treatment or soil application. The present study was undertaken with a view to evaluate the effectiveness of azodrin, bidrin and dimecron (phosphamidon) against the red cotton bug attacking okra plants by applying the compounds to stems with dosages comparable to those of field application.

**Methods and Materials**

The following insecticides were tested against the red cotton bugs: Azodrin (3-hydroxy-N-methyl-cis-crotonamide dimethyl phosphate), Bidrin (3-(dimethoxyphosphinoyloxy)-N, N-dimethyl-cis-crotonamide) and Dimecron (2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate). The technical procedure was very much the same as outlined by Bariola *et al.* The okra plants were grown singly in 12 in diameter earthen pots. When the plants attained a height of 12–15 in they were used for the experiment. For each of the insecticides dosages of 10.0, 5.0 and 2.5 mg of active material per plant were used. The 2.5 mg/plant dosage approximated 0.25 lb/acre assuming 3 plants/ft of row in a field. The testing pots were arranged at random. The insecticide in acetone was applied to the stem of each plant on a band of thin cloth 2 in wide around the main plant stem about 2 in above the soil level with the help of a pipette. Two series of tests were done. In the first series the bugs were confined in small wire cages, 1½ in diameter and 5 in long, that enclosed the apical leaves of the plants. Both sides of the cage were closed with the help of cotton so that the insects could not come out. Each cage was supported by a small bamboo stick. In the second series the bugs were confined to the entire plant in wooden-frame wire cages, 10 in diameter, in such a way that no insect could come in contact with the insecticide applied area of the stem. The two sides of the cage were covered with thin cloth so that no insect could escape. The clothes were bound firmly by threads. Ten adult insects of equal size and approximately of same age were used for each test and was replicated 10 times. Acetone-treated control was included in each test. Similar tests were also done with the third instar nymphs. Mortality counts were made 72 hr after the release of the insects to the plants. Percentage mortality was corrected by using Abbott's formula. A factorial analysis of variance and Duncan's multiple range test was utilized to test for significance of the means at the 5% level.

**Results and Discussion**

The data have been summarized in Tables 1 and 2. The two series of tests with both the adults and nymphs showed some differences in the percentage of mortality after the indicated ex-
CONTROL OF COTTON JASSID EMPOASCA DEVASTANS, BY PETKOLIN AS COMARED WITH OTHER INSECTICIDES

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(Received May 21, 1969)

Petkolin, Sevin, Toxaphene, Dimecron, Diazinon, Endrin and Malathion were compared to evaluate their efficacy against jassids, Empoasca devastans on Cotton crop. Three lb active ingredient per acre Petkolin gave 84.51% mortality after 24 hr 90.7% after 72 hrs while 2 lb Toxaphene gave 76.0% and 80.0% mortalities after 24 hr and 72 hr respectively.

Maximum cotton yield of 17 maunds per acre was obtained with Sevin while Petkolin gave 14 maunds and in Toxaphene the yield was 12.13 maunds per acre.

The pesticidal potentialities of Petkolin have been reported earlier by Ashrafi et al. against cockroaches, housefly and mosquito larvae, locusts, and flour beetles in the Laboratory conditions and against different crop pests in West Pakistan. Petkolin showed very low mammalian toxicity against white rats and was nontoxic to the plants.

The present paper deals with the extensive field evaluation of Petkolin in comparison with Sevin, Toxaphene, Dimecron, Diazinon, Endrin and Malathion against jassids, Empoasca devastans, on cotton crop.

Materials and Methods

The experiment was laid out on 6 acres land in the Cotton Botanists Multiplication Area for variety of cotton to control jassids, Empoasca devastans.

The experiment was carried out on M-100 variety of cotton to control jassids, Empoasca devastans.

### Table 1. — Quantity of Insecticides Available in 2.5 Gallons Water when the Amount of Water per Acre was 20 Gallons, 30 Gallons and 40 Gallons.

<table>
<thead>
<tr>
<th>Insecticides</th>
<th>Qty. of insecticide/acre (a.i.)</th>
<th>% conc. (a.i.)</th>
<th>Amount of insecticide available</th>
<th>Qty. of insecticide in 4/5th of an acre</th>
<th>Qty. of insecticide in 2.5 gallons water when the amount of H₂O per acre was 20 gallons</th>
<th>Qty. 30 gallons</th>
<th>Qty. 40 gallons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Petkolin 40% E.C.</td>
<td>3 lb</td>
<td>0.3</td>
<td>7.5 lb</td>
<td>30 oz</td>
<td>435 ml</td>
<td>290 ml</td>
<td>217.5 ml</td>
</tr>
<tr>
<td>2. Sevin 85% W. P.</td>
<td>1 lb</td>
<td>0.1</td>
<td>1.2 lb</td>
<td>4.8 oz</td>
<td>69.6 ml</td>
<td>46.4 ml</td>
<td>34.8 ml</td>
</tr>
<tr>
<td>3. Toxaphene 80% E.C.</td>
<td>2 lb</td>
<td>0.2</td>
<td>2.5 lb</td>
<td>10 oz</td>
<td>145 ml</td>
<td>96.6 ml</td>
<td>72.5 ml</td>
</tr>
<tr>
<td>4. Dimecron 100% E.C.</td>
<td>4-6 oz</td>
<td>0.037</td>
<td>4.0 oz</td>
<td>1 oz</td>
<td>14.5 ml</td>
<td>9.6 ml</td>
<td>7.25 ml</td>
</tr>
<tr>
<td>5. Diazinon 60% E.C.</td>
<td>4-6 oz</td>
<td>0.037</td>
<td>6.6 oz</td>
<td>1.6 oz</td>
<td>23.2 ml</td>
<td>15.4 ml</td>
<td>11.6 ml</td>
</tr>
<tr>
<td>6. Endrin 20% E.C.</td>
<td>4-6 oz</td>
<td>0.037</td>
<td>20 oz</td>
<td>5 oz</td>
<td>72.5 ml</td>
<td>48.3 ml</td>
<td>36.25 ml</td>
</tr>
<tr>
<td>7. Malathion 57% E.C.</td>
<td>1 lb</td>
<td>0.1</td>
<td>30 oz</td>
<td>7.5 oz</td>
<td>108.7 ml</td>
<td>72.5 ml</td>
<td>54.3 ml</td>
</tr>
<tr>
<td>8. Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Quantities of insecticides available in 2.5 gallons water when the amount of water per acre was 20 gallons, 30 gallons, and 40 gallons.
TOXICITY OF PETKOLIN-M IN COMPARISON WITH OTHER PESTICIDES AGAINST COTTON JASSIDS IN HYDERABAD REGION

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Petkolin-M alone as well as in combination with Methyl-parathion (Petkolin-MN₁) and Diazinon (Petkolin-MN₂) gave effective control of mites and jassids on cotton crop. Petkolin-M, Petkolin-MN₁ and Petkolin-MN₂ killed 91%, 100% and 100% mites respectively. Petkolin-M, Petkolin-MN₁ and Petkolin-MN₂ gave 93% to 94%, 100% and 100% mortality of jassids respectively after 24 hr of treatments. Petkolin-M was found compatible with Methyl-parathion and Diazinon.

In recent years, Petkolin has been tested against a variety of agriculture pests like mites, cotton leaf roller, sugar-cane pyrilla, maize borers, date palm scales, pink boll worm, rice borers, aphids and has been found effective to control them. The effective dosage has been found to range from 1.6 lb to 3 lb active ingredient per acre. Later on Petkolin was modified by adding 1% additive in petroleum before subjecting it to the process of chlorination and it was named as Petkolin-M.

Petkolin-M was found more effective than Petkolin against insects in laboratory as well as in field conditions and safer than many other chlorinated pesticides. Therefore, it was decided to test its efficacy alone as well as in combination with other pesticides on large scale in the field against mites (Tetranychus telarius (L)) and jassids (Empoasca devastans) attacking cotton crop. The experiment was conducted two months earlier before picking at the time when jassid and mite population was on the peak due to favourable conditions of humidity and temperature.

The pesticides used were Petkolin-M, Petkolin MN₁ (Petkolin-M (2 lb) + Methyl-parathion (0.25 lb), Petkolin MN₂ (Petkolin-M (2 lbs) + Diazinon (0.25 lb), Toxaphene, containing 14% Methyl-parathion, Diazinon, Methyl-parathion and Dimecron. The experiments were conducted on two sets of plots measuring 0.12 acre and half an acre to determine the effective toxic dose of Petkolin-M alone and in combination with Methyl-parathion and Diazinon in Hyderabad region.

Materials and Methods

In order to determine the efficacy of different pesticides against jassids and mites on cotton, two sets of experiments were designed. In the first set the plot-size was kept 0.12 acre and in the second half an acre.

First Set.—In the first set each treatment was replicated 3 times. Knapsack power sprayer was employed for the spraying. 3 lb active ingredient of Petkolin-M and 2.25 lb active ingredient both of Petkolin MN₁ and Petkolin MN₂ were used. Pesticide emulsions were sprayed uniformly on the crop. Pretreatment observations of mites and jassids were recorded on 20 different leaves taken at random from each plot. Posttreatment observations after 24 hr and 48 hr were taken in the same way.

Second Set.—Large scale field trial of Petkolin-M, Petkolin MN₁, Petkolin MN₂, Toxaphene, Methyl-parathion, Dimecron and Diazinon was conducted against jassids (Empoasca devastans) on cotton crop in Hyderabad region. An area measuring 16 acres was selected for the purpose. The area was divided into 32 sub-plots of ½ acre each. Layout of the experiment was randomised block design with four replications.

Petkolin-M, Petkolin MN₁, Petkolin MN₂, Toxaphene, Methyl-parathion, Dimecron and Diazinon were used at the rate of 3 lb, 2.25 lb, 2.25 lb, 2 lb, 12 oz, 8 oz and 12 oz respectively. Jico minor power sprayer with a tank capacity of 15 gallons was used for spraying. Great care was taken to avoid contamination of one pesticide with the other by washing the tank each time before using it again. Pesticides were sprayed in such a way as to give a thorough cover of the pesticide emulsions to plants. Pretreatment observations of jassid population were recorded by counting the number of jassids on 50 leaves of each treatment taken after 24 hr, 48 hr and 72 hr of spraying. The mortality percentage of each treatment was calculated separately.

Results and Discussion

Results of the experiments conducted showed that Toxaphene, Methyl-parathion, Dimecron, Diazinon, and Petkolin-M alone as well as in
SYSTEMIC CONTROL OF RICE BLAST CAUSED BY PIRICULARIA ORYZAE CAV.

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(Received March 3, 1969)

Thirteen fungicides were tested to evaluate their merits in systemic control of rice blast. Blasticidin-S and PMA (Phenyl Mercuric Acetate) were found to act systemically and they significantly reduced both the number and size of lesions found at sites relatively distant from the point of application.

Blasticidin-S, Du-Ter W-50 (Triphenyl tin hydroxide) and PMA acted as eradicants when they were applied at the pin-head stage of development of lesion. These fungicides did not kill the internal mycelium nor could they reduce the viability of the conidia but they retarded lesion development and controlled leaf blast by reducing sporulation nearly two fold. A new experimental product, Fungicide 1991 also found to control blast systematically.

Numerous attempts have been made to control blast. Extensive research on blast ecology, resistance and on methods of control, has been conducted in Japan. Control of disease by systemic fungicides is the most efficient and is certainly the most appealing. The systemic toxicant must be absorbed by the plant and translocated to different parts. Various greenhouse methods have been devised to evaluate the systemic action of candidate fungicides. Potted plants may be watered for a few days with a fungicide solution or the seedlings may be allowed to stand in solution for 2 to 3 weeks prior to inoculation.

Eradicative fungicides permit control of diseases after infection has taken place; this is highly desirable. Eradicative fungicides must be systemic. Keitt and Jones were to report that distinct inhibition of scab development was possible when the mixture of lime-sulphur and arsenate of lead was applied 24 hr after the infection period began. The possibility of the use of so-called eradicative spray for scab control was thoroughly explored in the greenhouse studies on potted apple trees by Hamilton. Since then various workers have done much to expedite the use of eradicative fungicides against many diseases. In Japan, Misato et al. demonstrated that greenhouse grown rice plants when sprayed with a solution of Blasticidin-S 1 or 2 days after inoculation with the spore suspension of Piricularia oryzae, fewer lesions were detected on the leaves. He also reported that Blasticidin-S was more effective than PMA as a curative fungicide.

In the second test, 18-day old rice seedlings were dug up and washed in water. Seven seedlings were transplanted into a pint Mason jar containing the fungicidal preparation. The seedlings were kept erect by 2 wire nets, one at the mouth and the other approximately 3" lower. For a better estimation of systemic action of the candidate fungicides, the plants were grown in the aqueous fungicidal preparations for 6 days prior to inoculation in order to maintain a continuous flow of the test materials into the plant tissue. The plants of each jar were inoculated by spraying 10 ml of the standard spore suspension per flat. These were kept in the humidity chamber for 36-48 hr. Each treatment was replicated 3 times with a water control. One week after inoculation the numbers of typical blast lesions, on the fourth plant leaf, from different treatments were compared. The percentage reduction (R) in blast lesions with test fungicides was calculated as follows:

\[ R = \left( \frac{C - T}{C} \right) \times 100 \]

where, C = Average number of lesions in the control

T = Average number of lesions in the treatment

Materials and Methods

The experiment was conducted at the Rice-pasture Research and Extension Centre, Beaumont, Texas, U.S.A. The systemic effect of the fungicides was evaluated in two tests. In the preliminary experiment 13 materials were included. Guflrose rice seedlings were grown in metal flats. The fungicides were applied at the 3-leaf stage until run-off occurred. Five to six days later the seedlings in the 4-leaf stage were inoculated by spraying 10 ml of the standard spore suspension per flat. These were kept in the humidity chamber for 36-48 hr. Each treatment was replicated 3 times with a water control. One week after inoculation the numbers of typical blast lesions, on the fourth plant leaf, from different treatments were compared. The percentage reduction (R) in blast lesions with test fungicides was calculated as follows:
Effect of Types of Seedling Nurseries on the Performance of Ten Cultivars Grown as Transplant Aus Rice

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Seedlings of 10 cultivars, namely, Dharial, Kataktara, Charnock, Dular, Marichbati, MIFB-322-1, Taichung (Native), IR8-288-3, IR5-47-2, and Peta, were raised in 3 different types of seedling nurseries—‘Floating’, ‘Normal’, and ‘Dapog’—and transplanted as aus crop at the age of 26 days.

Floating nursery was found to be the best type of seedling nursery for local cultivars, while the types of seedling nurseries had no measurable effect on the grain yield of the exotic varieties. A maximum yield of about 61 maunds of grains per acre was obtained in case of IR8 and IR5. Relatively lowest grain yield of about 38 maunds per acre was recorded in Marichbati and Charnock. Dharial, Kataktara, Taichung (native), and Dular were intermediate in grain production.

Aus rice in East Pakistan is usually grown as a directseeded broadcast-sown crop. Experimental evidences indicate, however, that aus rice can also be grown as a transplant crop. For at least two reasons, growing of aus rice as a transplant crop is advisable provided irrigation water is available. Firstly, in growing aus rice in the normal way the cost of weed control by hand is excessively high and, with irrigation water available, this cost may be considerably reduced by growing the crop as a transplant one. Cost of water is likely to be lower than the cost of hand weeding. Secondly, the high yielding exotic cultivars of rice that have been brought into the country, especially from IRRI, seem to be better suited to transplantation than to direct seeding. Higher yield in transplant crop than direct seeded broadcast crop has been explained to be primarily due to better plant spacing in a transplant crop.

Seedlings for transplant rice are raised in different ways in different rice growing countries of the world. While growing seedlings on a seedling nursery on land, wet or dry, is the most widely used normal method of seedling raising in most of the rice growing countries, a type of seedling nursery, called ‘Dapog’, is extensively used in some parts of the Philippines. Again, ‘floating’ type of seedling nursery made on water bodies like ponds, tanks, and beels, is also occasionally used in some areas of East Pakistan. The results reported in this paper were obtained by growing ten selected exotic and local cultivars of rice as a transplant aus crop with seedlings raised in three types of seedling nurseries, Floating, Dapog, and Normal.

Materials and Methods

The experiment was conducted at the Agronomy Field Laboratory of the East Pakistan Agricultural University. The experimental field belonging to the Bramaputra Alluvial Soil tract of East Pakistan, was a medium high land with silt loam soil having a pH range of 6.6 to 6.8. Five local cultivars, namely, Dharial, Kataktara, Charnock, Dular, and Marichbati and 5 exotic cultivars, namely, MIFB-322-1, Taichung (native) 1, IR8-288-3, IR5-47-2, and Peta were included in the present study. Seedlings of all the rice cultivars were raised in 3 different types of seedling nurseries—Normal, Floating, and Dapog.

Normal seedling nurseries were made in drums (dia 23 in, height 18 in) filled up with well prepared loamy soil. The soil in the drums was fertilized with urea, treble superphosphate and muriate of potash to apply 28 lb N, 12 lb P (element) and 30 lb K (element) per acre in addition to 4.4 tons of cowdung. The manure and fertilizers were thoroughly mixed up with the upper 6 in of soil. Cowdung was applied 7 days before sowing and the fertilizers were applied 2 days before sowing the seeds in the nursery. Threeday sprouted seeds were then sown in the nursery on 25-4-1968 and the seeds were covered with a thin layer of soil to avoid drying. The nursery was irrigated as and when necessary until the seedlings were uprooted for transplantation in the crop field.

In the case of floating seedling nursery, a floating bed was prepared with bamboo matting placed on a raft of banana stems floating on water in a pond. The bed was plastered with a layer (1.5" thick) of mud rich in humus. Three-day sprouted seeds were then sown in the bed on 25-4-1968. Care was taken so that the seed bed remained just on the surface of water and that the bed did not hold standing water on it. No manure and fertilizer were applied in the seed bed.

For the purpose of raising rice seedlings in Dapog method, a compact, levelled, and flat bed
PREPARATION AND NUTRITIONAL EVALUATION OF HIGH PROTEIN BREADS CONTAINING OILSEED PROTEIN CONCENTRATES

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(Received January 11, 1969)

Breads were made containing protein concentrates prepared from cottonseed, rapeseed and groundnut cake. Skim milk powder and certain vitamins and minerals were also added to improve the nutritive value of the breads. Nutritional evaluation of the breads showed that the breads containing blends of oilseed protein concentrates and skim milk powder were found to be much better in all respects than that made of wheat flour and were slightly inferior to that containing skim milk powder alone.

In earlier communications\(^1\)\(^2\)\(^3\) preparation and biological evaluation of oilseed protein concentrates has been reported. They possess a bland taste and permit ready blends with cereal flours without having any deleterious effect on their physical properties. Because these are concentrated source of protein, addition of a small quantity is required to step up the protein content of the material. However, it was observed that a blend of oilseed protein concentrate with animal proteins, such as fish protein concentrate or skim milk powder, gave a higher net protein utilization value than using the oilseed protein concentrate alone because of mutual supplementation of deficient amino acids in the two proteins. It was, therefore, considered desirable to utilize blends of oilseed protein concentrates and skim milk powder in enriching wheat flour.

Because of its easy digestibility leavened bread is becoming our important diet particularly in the diets of children, invalids and convalescents. Bread enrichment has been carried out for a number of years in many countries of the world. The protein nutritional value of the bread has been improved by the addition of skim milk powder, soy flour, fish flour, lysine and methionine elsewhere.\(^4\)\(^5\)

It will be of great value to produce an enriched bread with necessary vitamins, minerals and enough protein to take care of nutritional requirements of vulnerable groups of the population.

In preliminary trials with these protein concentrates several formulae were tried. It was observed that incorporation of 7-8% of the protein mixture does not appreciably affect the baking properties of the dough. The high protein bread was similar to unfortified control bread with respect to loaf volume, texture, appearance and taste. Preliminary calculation of protein score and net dietary protein calories % (NDP cals %) according to the method of Miller and Payne\(^6\) showed that the breads would yield an NDP cals % of about 8, which is considered suitable for young children,\(^7\) hence no attempt was made to further increase the amount of protein mixture in the bread. The present report deals with the preparation and nutritional evaluation of these enriched breads along with breads (1) containing skim milk powder and (2) wheat flour only to serve as controls.

Materials and Methods

Protein concentrates from indigenous cakes were prepared according to the methods described earlier.\(^2\)\(^3\) Since commercial groundnut cake contained a lot of hulls groundnut protein concentrate was prepared from dehulled and defatted groundnuts in the laboratory. The protein content of cottonseed, rapeseed and groundnut protein concentrates as determined by semimicro-Kjeldhal method were 76.0, 70.0 and 92.0% respectively.

Good quality skim milk powder (protein 35%) was obtained through the courtesy of Dr. S.M.K. Wasti of Mayo Hospital, Lahore. Other ingredients were purchased locally.

Preparation of Breads.—Water (220 ml) was added to Baker’s yeast and the suspension was allowed to stand for 10 min. Sugar and salt were dissolved in another lot of 200 ml water. The remaining dry ingredients, i.e. wheat flour, skim milk powder, protein concentrate, vitamin and mineral mixture were mixed together and the above two mixtures were added to dry mix and made into a dough with the addition of required quantity of water, i.e. 200–220 ml, determined earlier by Farinography. The mixed dough was fermented for 4–5 hr at 80°F and then the desired amount of dough was added to the mould pan and placed for another hour at 95°F. The dough was baked at 400–450°F for ca 40 min.
CHEMICAL COMPOSITION OF GUAVA AND BANANA FRUITS GROWN IN HYDERABAD REGION

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(Received May 27, 1969)

Chemical composition of five varieties of guava and two varieties of banana fruits was determined. The data showed that the varieties V4 and V5 of guava fruit had more total sugars, vitamin C and protein contents, while Basrai banana was found to be richer in non-reducing sugars, proteins and vitamin C contents than the rest of the varieties under study.

Fruits play a very important role in the balanced nutrition of man and are, therefore, essential in our daily diets. Banana and guava are among the most important fruit crops grown in the Hyderabad Region. They are rich in carbohydrates, minerals and vitamins and are, therefore, considered to be very nutritious and cheapest source for these ingredients.

Although considerable work has been done elsewhere on the moisture, ash, acidity, sugars, crude fat, crude protein, and vitamin C contents of these fruits, yet no detailed information is available about the various constituents in different varieties of these fruits grown in this part of the province.

An attempt has, therefore, been made in the present studies to assess the nutritive value of different varieties of guava and banana fruits grown in the Hyderabad Region (West Pakistan).

Material and Methods

Five varieties of guava (V1–V5) and two varieties of banana (Basrai and local) fruits were taken for the present study.

The following varieties of guava fruit selected on the basis of some of their physical characteristics mentioned below were taken for the present study:

**Variety No. 1:** Diameter 4.5 cm; round in shape; centre completely full of seeds.

**Variety No. 2:** Diameter 4.9 cm; long in shape; centre completely full of seeds.

**Variety No. 3:** Diameter 5.5 cm; round in shape; moderately full of seeds.

**Variety No. 4:** Diameter 7.3 cm; oval in shape; fairly seeded.

**Variety No. 5:** Diameter 7.8 cm; round in shape; sparsely seeded.

The chemical analysis of the fruits was done by the standard methods of analysis six times in each case to minimize the experimental error.

**Results and Discussion**

The mean values obtained in case of each estimation regarding the chemical composition of guava and banana fruits are given in Table 1 and discussed separately in the following pages under each fruit:

**Guava Varieties.**—From the data it appears that the variety V5 in case of guava fruit had the highest moisture and lowest dry matter contents. The highest dry matter content was however found in variety V1.

The ash content of guava varieties indicate that the mineral matter content was highest in V1 (0.68%) followed by V2, V3, V4 and V5 varieties. The reports of Chughtai et al. and Hayes showed lower values of the ash contents, while Watt and Merrill reported higher values. In the present investigations the difference in the results of ash contents may be due to different soil and climatic conditions under which the fruit crops were grown.

Reducing sugars were highest in variety V4 (6.79%) while in case of other varieties, it was in the order of V5>V3>V1>V2. Non reducing sugars were found to be highest in variety V5 (2.22%), while in case of other varieties, these values were in the order of V2>V3>V1>V4. Total sugars on the contrary were highest in variety V5 (18.15%), followed by V4>V3 V2>V1.

The pH values in all the varieties ranged from 4.6–4.8 while acidity percentage ranged from 0.42 to 0.56%.

The observations with regard to crude protein contents showed that the values ranged from
THE STAPHYLINDIAE, COLEOPTERA OF PAKISTAN

Part III.—A key to the genera and species of the Piestinae, Osoriinae, Pseudopsinae and Oxytelinae, with descriptions of new genera, subgenera and species from Karachi.

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Introduction

Little is known about the bionomics of the staphylinid beetles treated in this paper. As far as the habits are concerned, the following associations are established: *Eupiestus Kraatz, 1859*—dead leaves or other vegetable debris, moss, etc.; *Siagonium* Kirby and Spence, 1815—under the bark of trees; *Holosus* Motschoulsky, 1857—in decaying tree-trunks; *Tetrapleurus* Bernhauer, 1914—subcortical; *Elesis* Castelnaud, 1835—subcortical; *Leptochirus* Germ., 1823—subcortical, feeding on woody fibre; *Osorius* Latreille, 1829 in decaying tree-trunks, also on the sandy banks of streams; *Mimagonus* Fauel, 1903—in rotten tree trunks, also in tobacco; *Holotrichus* Erichson, 1840—in decaying tree trunks; *Planestomus* Jacq. du Val, 1859—in damp places in galleries, frequently attracted to light, *Anycrophorus* Kraatz, 1858—near water; *Carpelinus* Samovale, 1819—*Trogophloeus* Mannheim, 1830—in damp places and near water; *Oxytelopsis* Fauel, 1895—in debris and damp places; *Delopstis* Fauel, 1895—in damp debris; *Oxylens* Gravenhorst, 1802—in dung, coriaceous, elytra pitchy, posterior margins of the abdominal segments narrowly Rufescent, antennae and legs reddish testaceous *P. bistriatus* (Fauel, 1895) Cameron, 1930

3. Abdomen striate at the sides; maxillary palp with the fourth segment elongate; more or less convex species with the facies of certain Tachyporinae *Holosus* Motschoulsky, 1857 elytra sparingly obsoletely punctate

*H. brevipennis* Fauel, 1904

Abdomen rarely striate at the sides; maxillary palp with the fourth segment less elongate; more or less parallel, depressed or sub-depressed species; middle and posterior tibiae finely spinose or setose externally *Lispinus* Erichson, 1840

4. Pronotum without median impressions before the base, lateral impressions broader and less deep; pronotum less finely and more closely punctured; elytra less sparingly punctate

*L. quadricollis* Cameron, 1924

Pronotum with more or less distinct median impressions

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1. Elytra each with four keels, the sutural and the humeral united in an arch behind the the discal ones *Tetrapleurus* Bernhauer, 1914 vertex of head not sulcate, rather closely and coarsely punctate like the rest of the surface

*T. himalayicus* Cameron, 1924

Elytra without such keels

2. Tarsi 5-segmented; elytra without sub-humeral stria

3. Tarsi 4-segmented; elytra with a fine stria passing from the shoulder to the apical border *Pseudolispinus* Bernhauer, 1926 black moderately shining, coriaceous, elytra pitchy, posterior margins of the abdominal segments narrowly Rufescent, antennae and legs reddish testaceous

4. Pronotum without median impressions before the base, lateral impressions broader and less deep; pronotum less finely and more closely punctured; elytra less sparingly punctate

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SHORT COMMUNICATION  
BIOLOGICAL SCIENCES SECTION


CRITICAL OXYGEN LEVEL FOR THE RESPIRATION OF LYCOPERSICON ESCULENTUM

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Technology Section


QUALITY AND CHARACTER OF PAKISTANI WOOLS

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Five different series of Pakistani wools, of both carpet and medium type, were examined for a number of fibre characteristics. The relationship between crimp and diameter was investigated with a view to examining its use for quality assessment. The relationships among the various other parameters and especially the dependence of character on other characteristics were also investigated.

Pakistani wools are known at home and abroad for their suitability for carpet manufacture. These wools, however, differ widely in their origin as they come from as many as 22 breeds of sheep. A survey of the fineness of the wools has revealed that some of them are as fine as 50's, whilst same individual fleeces approach 60's. A substantial portion of these wools gets mixed up with coarse carpet types and is not utilized for its proper end use. This is partly because of the fact that no system for quality assessment of these wools by eye and hand methods, analogous to well-known systems used for fine wools such as Merino, seems to have evolved. Some of the reasons for this situation could well be the low crimping commonly associated with these wools and their general classification as carpet wool with little or no emphasis on fineness within the type.

An additional factor has been introduced to this situation in the past 10-12 years. Attempts have been made at crossbreeding some of the breeds producing medium quality wools with imported fine woolled breeds such as Rambouillet. As a result, some quantities of medium and fine quality wool are now being produced.

The practice of visual assessment based largely on observation of staple crimp frequency is not very accurate as there are sufficient individual exceptions to the relationship between diameter and staple crimp to make it unsatisfactory to place full reliance on the frequency. The desirability of more objective techniques has, therefore, been long expressed. The visual assessment would, however, continue to be of significant assistance till such time that alternative objective techniques of almost equal convenience become established. Further, in situations such as above where mainly the matter of distinguishing medium quality wools from coarser carpet types is involved, the method could be of sufficient effectiveness.

Most characteristics of wool associated with visual appraisal such as colour and length, are directly observable and offer little or no difficulty in the assessment. The estimation of quality or fineness is perhaps the most critical aspect, partly because of its importance and partly because of the difficulty of its accurate assessment by the method. Another such critical characteristic is the 'style' or 'character' of wool which affects the price and even if a direct premium is not paid for a wool of good character, its general attractiveness is likely to influence the buyers' evaluation. The causal factors for character are not fully known even in the case of Merino wool, despite such attempts as those by Sidey, Lang and Lockhart. Pakistani wool, especially of the carpet type, constitutes a special system where some fibre characteristics are at marked variance with those of Merino wool and, therefore, offer an opportunity for investigation of their inter-relationships in comparison to the known facts.

In addition to the above, there are other considerations necessitating an investigation of the said relationships. Shah and Whiteley have shown that, in terms of their substance as reflected through their mechanical properties, carpet wools do not significantly differ from fine wools and reasons for their particular end use should, therefore, lie largely in their external parameters.

The objectives of the present study were thus to examine the external parameters of carpet wools, with special emphasis on quality crimp relationship, analysis of 'character' and other interrelationships among the various parameters.

The term medium quality wool has been frequently used in this study to denote indigenous wools finer than 44's to distinguish them from the coarse carpet types.
COMPOSITION AND MECHANICAL PROPERTIES OF PAKISTANI WHITE AND YELLOW SILK

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Amino-acid composition and mechanical properties of Pakistani white and yellow silk fibroin have been determined. The yellow variety, associated with higher mechanical constants, was rich in alanine, but poor in tyrosine and phenylalanine.

Investigations on composition and mechanical properties of protein fibres, wool and silk, have been of significant assistance in revealing information about their structure. The work on the structure of silk fibroin has been reviewed by Howitt.\(^1\) That the results obtained by the various workers for the amino-acid make up of silk do not totally agree with one another is not surprising in view of both the differences in the techniques of analysis as well as the natural variation associated with most biological products.

Two varieties of silk (Bombyx mori), white and yellow, are grown in West Pakistan. The present study is aimed at a comparison of the mechanical properties of these two varieties vis-a-vis their amino-acid composition.

The desirability of utilizing several solvent systems for paper chromatographic analysis of protein has already been expressed.\(^2\)\(^3\)\(^4\) An additional aim of the present study is to elucidate a solvent system for such an analysis conducive to obtaining effective separation of the spots and results of acceptable precision.

Materials and Methods

Samples.—Samples of white and yellow mulbery silk cocoons were obtained from the Sericulture Department, Peshawar.

Reeling.—The silk was reeled by steeping the cocoons in a boiling water-bath for 1-2 hr and the free end of the filament was drawn.\(^5\)

Degumming.—The reeled silk was degummed by the soap-alkali process.\(^6\) Each sample was dried at 140°C for one and a half hour before proceeding with subsequent procedure.

Hydrolysates.—Method adopted was essentially that of Baker and Khan.\(^7\) 250 mg of silk were treated with 5 ml 6N HCl in a pyrex glass test tube for the preparation of the acid-hydrolysate. The tube was sealed and heated at 110°C in an electric oven for 36 hr. The tube was cooled, the seal broken and the hydrolysate evaporated to dryness under vacuum over calcium chloride and sodium hydroxide. The residue was dissolved in distilled water and the solution evaporated to dryness a number of times. This was then dissolved in 2 ml 10% isopropanol and filtered. The residue was thoroughly washed with 10% isopropanol. Finally the pH and the concentration (mg silk/ml) of the hydrolysate were adjusted to the desired value as given in Table 1.

For the preparation of alkali hydrolysate 250 mg of the silk were treated in a glass tube with 1.4g of recrystallised barium hydroxide and 10 ml of distilled water at 120°C for 24 hr. The tube was then cooled and opened and the barium hydroxide neutralized with sulphuric acid. The precipitate of barium sulphate was removed by filtration and was washed four or five times with hot water containing 2 drops of glacial acetic acid per litre. The washings were added to the hydrolysate and the volume reduced to approximately 1 ml by evaporation in a current of hot air. Complete drying was effected in a desiccator over calcium chloride and sodium hydroxide. The dried hydrolysate was dissolved in 5 ml of 10% isopropanol, the pH of the solution was adjusted to 7.0-7.5 and the volume adjusted to 10 ml. Only tryptophane was determined in the alkaline hydrolysate.

Colour Reagents.—Three colour reagents were prepared as described below:

(i) Ninhydrin Reagent No. 1: five grams of ninhydrin were dissolved in 100 ml n-butanol and 50 ml glacial acetic acid. This solution was added to water-saturated n-butanol. The latter was prepared by mixing 1000 ml of n-butanol with 500 ml of water and shaken in a separatory funnel. The aqueous layer was removed.

(ii) Ninhydrin Reagent No. 2: For the preparation of this reagent the same method was used as for reagent No. 1, except for the fact that 25 ml of glacial acetic acid were used instead of 50 ml.
RESILIENCE CHARACTERISTICS OF PAKISTANI WOOL

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Resilience or percentage recovery characteristics of 6 different types of Pakistani wool i.e. Lohi-Harnai, Hashtnagri, Dumba, Kaghani and Azad Kashmir have been studied using a small cylinder with pistons and applying pressure on a definite weight and volume of wool pellets. Percentages of recovery have been recorded at various intervals of time. The first 4 breeds have almost 100 percent recovery after 24 hours while the latter two breeds covered a period of 48 to 72 hours. Possible effect and relation of fibres length, diameters and tensile strength of each of the six breeds with percentage recovery have been observed and the importance of it in woollen apparel cloth and specially in carpets, manufactured from Pakistani wool, has been discussed.

Pakistan produces mostly carpet wool which is quite suitable for manufacturing carpets, having the characteristics of ideal carpets. Majority of wool is exported, but considerable quantity of it is utilized within the country for manufacturing machine and mostly hand-made carpets. In 1967-68 traditional hand-made carpets worth Rs. 30,483,000 have been exported. Hand-made carpets of Pakistan are appreciated abroad for their shape, drape gracefully and do not wrinkle easily. In Pakistan majority of wool produced within the country is utilized in carpet manufacture and very little quantity of it is consumed in woollen cloth manufacture.

Our present study deals with the resilience or percentage recovery characteristics of Pakistani carpet wool. But some fine quality carpets are also manufactured from fine wool produced within the country, therefore, we have included two Pakistani fine wool breeds in our study for the comparison of piles recovery. The present work deals with the resilience or percentage recovery characteristics of different types of Pakistani wool already categorized as ideal carpet wool and utilisation of it in low to medium type woollen cloth as medullation and strength point of view.

Material and Method

Ten samples each of Lohi, Harnai, Hashtnagri, Dumba, Kaghani and Azad Kashmir wool breeds have been selected at random from the big lots of each of the above breeds. All these samples were scoured and their residual matters determined according to ASTM standards (D-584-53T).

Residual Matters.—All the samples were hand dusted thoroughly. The scouring solution contained 0.3% sodium carbonate and 0.1% surf a textile scouring detergent. The samples were scoured in 'malmal' bags made from a country made fine cotton cloth. In order to avoid felting in the scouring solution in the hand scouring machine maintained at 33°C. The scoured samples were rinsed in the hydraulic rollers and dried in the oven at 105°C to 110°C.

Fibre Length.—The length was measured by stretching the fibres on a black velvet board against...
COMPARISON OF FELLMONGERED AND SHORN WOOL

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Samples of fellmongered wool, collected from a fellmongering firm in Lahore have been examined. The important fibre characteristics such as mechanical properties, felting, friction and dyeing of the wool have been evaluated and compared with shorn wool. No significant differences could be detected in these characteristics between the two types of wool.

Skin or fellmongered wool refer to the wool removed from the skin of slaughtered sheep by the process of fellmongering. This wool comprises about 10 percent of the world wool supply and is considered to be inferior to shorn wool. The industry is a world wide one, with France being the largest processor of skin wool. The two main products of fellmongering are the wool (called slape wool, if unscoured and skin wool after scouring) and the de-woolled skin or pelt.

Sheep skins can be classified broadly into fine-woolled types such as that of Merino and coarse-woolled such as that of Lincoln and carpet type. The pelt of the former type is thin and has little commercial value while that of the latter is thicker, denser and consequently more valuable for leather making. It is evident that as far as fellmongering practice is concerned, it is practically impossible to lay down rigid rules, because the raw material, climatic conditions and plant layout all may vary significantly. Moreover, the fellmongering techniques used in a particular country depend on whether the pelt or the wool is the more valuable commodity. The effect on wool of the various fellmongering processes is also controversial.

In Pakistan no work seems to have been done on the local fellmongering practice. The present study aims at elucidating whether the methods applied here for de-woolling affect the wool characteristics. Thus in this paper important fibre characteristics such as mechanical properties, felting, friction and dyeing behaviour of skin and shorn wool have been investigated and compared.

Materials and Methods

Wool Samples.—The wool samples were collected from a fellmongering firm in Lahore. The skins of slaughtered sheep are brought over from various parts of West Pakistan to Lahore for fellmongering. Samples of shorn wool from inside of the skin were taken from each of the 10 skins before fellmongering process. The samples were again taken after fellmongering process from the same vicinity. The samples were cleaned with petroleum ether and then with alcohol followed by water and the following studies were made on these wools.

Mechanical Properties.—A Schopper dynamometric apparatus (constant rate of loading) was used for finding breaking strength and percent elongation. One end of the single fibre was suspended from the upper clamp of the hydraulic type testing machine, while the pretension (200mg) was suspended freely from the other end of the fibre and then tightened. Measurements were made at about 21°C and 65% R.H.

Frictional Properties.—Lipson's method was employed to determine the directional frictional effect (D.F.E. and scalines of dry fibres (21°C and 65% R.H.) and wet fibres (0.1N HCl) of skin and shorn wool. Ten fibres were withdrawn at random each from true, heterotypical and medullated fibres from each sample and the following techniques were adopted.

Each fibre was suspended on a cylindrical rod of polished horn and a hook weighing 0.2 g was attached to each end. Small weights were added on one side, so that slippage occurred, when the difference in tension $T_1-T_2$ reached a critical value. The frictional coefficient is then given by

$$\mu = \frac{1}{\theta} \log \frac{T_1}{T_2}$$

where $\theta$ is the angle of contact between fibre and cylinder and in this case $\theta = \pi$ radians. Difference in frictional coefficients with and against the scales ($\mu_1-\mu_2$) gives D.F.E., whilst scaliness has been defined by Speakman to be

$$\text{Scaliness (\%)} = \frac{\mu_1-\mu_2}{\mu_2} \times 100$$

Felting Properties.—Exactly one gram of scoured, carded wool, conditioned at 21°C and 65% R.H. was put in a bottle which contained 0.1N HCl with one drop of non-ionic detergent. After shaking for one hour, the ball was rinsed several times with distilled water. The volume of the
SCIENTIFIC GRADING OF JUTE

Part III.—Determination of Lignin of Different Grades of Jute

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(Received April 22, 1969)

The lignin content of different new grades of white (Corchorus capsularis) and Tossa (Corchorus olitorius) jute has been found to increase from higher to lower grades of jute. The average lignin content of Tossa is less than the white variety. The findings of the present investigation indicates that lignin content may be correlated with grading of raw jute.

In our previous communications we have presented some results on (a) Lustre determination and (b) Cross and Bevan Cellulose of different new grades of Pakistani jute for grading them on scientific basis. In this paper we are presenting the lignin content of both White and Tossa varieties of jute, which may be used as another favourable and acceptable index for grading of jute.

Lignin is an integral constituent of jute fibre. Chemically speaking lignin is made up of large, basic repeating units involving a not too well understood combination of C₆ to C₃ units. It is fairly established that the C₆ units are basically benzene nucleus as compared to the anhydro-glucose units of cellulose chains, which is the main component of jute fibre. Lignin is virtually noncrystalline, and is not a single compound, but is probably mixture of related compounds bonded to the cellulose chain of jute. The sulphuric acid lignin, resulting from the analytical removal of cellulose from jute with 72% sulphuric acid, is only partially soluble in organic solvents, such as, methyl and ethyl alcohol, acetone, formic and acetic acids, methyl and ethyl acetates, pyridine, chloroform and dioxane. Pulping process on the other hand dissolves the lignin and other components of jute in the alkaline reaction mixture, leaving primarily cellulose as the pulp. The lignin obtained by acid precipitation of such alkali lignin is different in properties to that of the acid lignin. For the present investigations it was considered proper to investigate analytically the sulphuric acid lignin of jute for establishing a favourable index for grading of jute. Normally, it will be expected that the inferior quality of jute will contain more lignin and in practice the lowest grade of jute as well as the stem portion of jute known as jute cuttings when separated contain the largest amount of lignin and have woody hard feel in patches. Some of these excess of lignin is present due to incomplete or partial retting thus relegating the jute fibre sample to a lower grade. Lignin is responsible for stiffness in fibre and “yellowing” of jute fibre and jute goods.

The lignin content of white (Corchorus capsularis) and Tossa (Corchorus olitorius) has been determined by sulphuric acid method from Pucca new grades of jute (defatted). Tossa variety has been found to contain comparatively low lignin value than white variety. This lower lignin content in Tossa and higher in white jute enables us to obtain marked and sharp inter-variety distinctions between them and also distinguish of the former from the latter. In both the varieties, the lignin is least in the top grade, while highest in the lowest ones. And in individual grade there is increasing trends of lignin distribution from top to the bottom. The higher lignin value at the bottom is mainly due to its over maturity, improper retting, harsh and stiffness in fibre in comparison with the middle and top portion respectively.

Experimental

The pucca graded bales were purchased through the Pakistan Jute Association.

Each jute sample was cut into bottom, middle and top portions and ground to fine powder of 60 mesh in grinding machine and finally defatted by extracting with methanol—benzene mixture (2:3). The residu was dried in oven at 110° to constant weight.

Dry jute powder (1.0 g.) was treated with 10 ml 72% sulphuric acid (3:4:5 (V/V) in an ice bath for about two hours with frequent stirring by a polished glass rod. The whole mixture was diluted by adding 200 ml of distilled water and refluxed in a steam bath for six hours. After cooling the mixture was filtered through a sintered glass crucible (Porosity No. 2) and washed exhaustively
study on the load-elongation curve at low extension of Kaghani wool fibres

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In order to study the tensile properties of dry and wet wool fibres of Kaghani wool, 50 samples were tested for breaking strength and elongation. Moreover, strength at 20% elongation as well as Hookean slope of dry and wet wool fibres, were determined in the case of the three types of fibres, i.e. true, heterotypical and medullated. The variations in cross sectional area were also examined and the relationship between the various parameters were pursued.

The behaviour of wool fibres as regards their ability to stretch when a load is applied to them and also to recover when unloaded is a subject of considerable practical interest, since wool fibres are subjected to frequent stresses of just this kind during processing as carding, combing and spinning etc.

Some work has been done in these Laboratories on the force and elongation at breaking point of Pakistani wool on dry fibres (65% R.H. and 20°C) only, but no attention has been given to the mechanical properties of wet wool fibres or at low extension. Since in practice the load is not so high which breaks the fibres, but rapid extension and contraction of the fibre occurs, a study at the low extension is more relevant to the practical conditions in processing. In the present study, 50 samples of Kaghani wool fibres were collected from the home tract of the Kaghani breed which extend from Balakot to Babusar top in the North-Western area of West Pakistan. This breed is considered superior to other Pakistani breeds due to its low medullation content.

If a wool fibre is loaded, it will extend by a certain percentage of its original length. The relationship between load and elongation can be determined experimentally, over a range of loads up to breaking point and expressed graphically as load-elongation curve. The present study is confined to the breaking force and elongation (%) of dry (65% R.H. and 20°C) and wet (immersed in distilled water for 24 hr) wool fibres. Major emphasis was placed on fibre before rupture i.e. 20% elongation. In this connection force at 20% elongation of dry fibres (F20 air) and wet wool fibres (F20 wet) as well as Hookean slope of dry fibres (H. air) and wet fibres (H. wet) of true, heterotypical and medullated wool fibres were recorded. The variation in cross-sectional area (A) was also determined and the relationships between the various parameters were examined.

Materials and Methods

The three types of fibres i.e. true, heterotypical and medullated were separated each from 50 samples of Kaghani wool with the help of benzene test. A Schopper dynamometer apparatus (constant rate of loading) which traces the load-elongation curve was employed. About 10 fibres were withdrawn at random from each sample and the length of the fibre was fixed at 3 cm. Breaking strength and elongation of dry (65% R.H. and 20°C) and wet wool fibres (immersed in distilled water for 24 hr) of true, heterotypical and medullated fibres of the 50 samples were determined. In another experiment, fibres of different cross-sections were extended to 20% and the force and Hookean slope determined. The fibre was immediately released and allowed to stand for 10 to 15 mins. Then it was immersed in water for 24 hr and the load-elongation curve was drawn. Thus force at 20% elongation of dry fibres (F20 air) and wet fibres (F20 wet) as well as Hookean slope of dry fibres (H. air) and Hookean slope of wet fibre (H. wet) were determined as explained by Burte. The diameter of the same fibre of 3 cm length was found at 15 points by a Lanameter (x500) and the cross-sectional area (A) calculated. The coefficient of variation (C.V.) was determined by the rapid method.

Results

Table 1 shows the mean breaking strength and elongation (%) of true, heterotypical and medullated dry Kaghani wool fibres. It is clear that the strength and elongation of medullated fibres have the highest values, while those of true fibres, the lowest. Table 2 shows breaking strength and elongation of wet wool fibres. As compared to dry fibres the breaking strength is slightly lower and elongation greater.

Table 3 shows √A, √F20 air, √F20 wet, √H. air, √H. wet and C.V. (√A) of true wool fibres,
STUDIES ON ADSORBENTS FOR THE PREPARATION OF CAROTENOIDS AND
CHLOROPHYLLS CONCENTRATES FROM BERSEEM (ALFALFA)

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The suitability of various locally available adsorbents for the preparation of carotene and chlorophyll concentrates from alfalfa has been studied. Sugar and starch have given the most promising results for the separation of carotenoids and chlorophylls. Regeneration of some of the adsorbents by solvent washing and drying at 85°C for two hours, for re-use, has also been investigated. Both sugar and starch may be used six times after regeneration before packing the columns.

Previously1,2 carotenoid content of various green plants and effects of dehydration and storage on the carotenoid content of berseem have been reported. Carotenoids and chlorophylls apart from being very useful natural food colours, are compounds of biological, medicinal and industrial importance. These compounds occur in substantial amounts in alfalfa, which is also very rich source of proteins. This highly nutritive plant may be processed to produce β-carotene (provitamin A) xanthophylls, chlorophylls and proteins. Proteins and carotenes thus isolated could be usefully utilized for vitamins A fortification and protein supplementation of foods to help in combating malnutrition in the country.

Carotene concentrates from chlorophyll—containing plant tissues can be prepared by different procedures. Recently adsorption chromatography3–7 has been used for the separation of carotenoids and chlorophylls. The aim of the present investigations is to study the suitability of locally available adsorbents for the separation of plant (berseem) pigments. The suitability of any adsorbent would depend upon its capacity to separate the carotenoids and chlorophylls, easy availability, low cost and easy regeneration for re-use.

No attempt has been made here to identify the different carotenoids and chlorophylls, and these have been estimated as β-carotene and total chlorophyll respectively. Treatment of the residue for the isolation of proteins would be dealt with in a separate communication.

Experimental

Chemicals.—Solvents used were of commercial grade. Talc and bauxite were indigenous materials. Calcium phosphates were prepared in these laboratories. Sugar, starch and sodium carbonate were obtained as commercial grade products. All adsorbents except alumina were passed through 36 mesh sieve and the fraction retained on 100 mesh was used. Alumina (Merck) was deactivated and used as standard. Unicam 600 was used for spectrophotometric estimation.

Procedure.—Berseem leaves were collected in the month of December and mixed well to get a composite sample. Extraction of pigments was done by the following procedures:

Procedure 1: It was essentially Kemmerer and Fraps8 procedure which has been described earlier.1

Procedure 2: Berseem leaves (10 g) were homogenized in 1:1 mixture of light petroleum (60–80°C) and acetone for five minutes in a Waring blender, in the presence of MgCO₃ (0.1 g), allowed to stand and decanted. The residue was again blended with solvent mixture for two minutes, filtered under suction, and the residue washed with the solvent mixture until the latter was colourless. Acetone was removed by washing with water, petroleum ether layer dried (Na₂SO₄) and made to a definite volume (500 ml) 10 ml of this extract was chromatographed on columns packed with different adsorbents. Carotenoids were eluted with light petroleum, eluate made to a definite volume and estimated spectrophotometrically in terms of β-carotene. The chlorophylls were eluted with 30:70 mixture of acetone and light petroleum. The solvents were removed under reduced pressure and the chlorophylls estimated according to the method of Comar and Zscheile.9 The results are recorded in Table 1. The concentrates are prepared by removing the solvents from the solutions of carotenoids and chlorophylls as obtained above, under reduced pressure.

Recovery of pure β-carotene by column chromatography using different adsorbents.

2 ml of standard solution of purified β-carotene (5 mg %) in light petroleum was chromatographed
CATION EXCHANGE CAPACITY OF SOME EAST PAKISTANI CLAYS

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Bejaipur clay occurs abundantly in a particular locality of the District of Mymensingh, and Mirpur clays (Red and Black) and Dacca river silt are also abundantly available in the District of Dacca, East Pakistan. Dacca river silt and Mirpur clays are locally used in the manufacture of bricks, tiles, etc., and Bejaipur clay is used for the manufacture of ceramic bodies by some ceramic industries of East Pakistan. Cation exchange capacity (c.e.c.) of these clays has been determined which also throw some light to the mineralogical composition of these clays.

A clay consists of a number of clay minerals. The chemical composition of these minerals is normally hydrated aluminim silicates resulting from weathering of igneous rocks. In water medium a clay particle behaves as a negatively charged particle and it is a polyvalent in nature. The electrical neutrality is maintained of these charged particles by a swarm of positively charged particles by a swarm of positively charged particles from aqueous solution. J.T. Way first reported his finding to the Royal Agricultural Society that soils were able to remove ammonia from weathering of igneous rocks. In water medium a clay particle behaves as a negatively charged particle and it is a polyvalent in nature. The electrical neutrality is maintained of these charged particles by a swarm of positively charged ions like Na⁺, K⁺, Ca²⁺, Mg²⁺, etc., cations are held by only feeble electrical forces and are easily replaceable by others. J.T. Way first reported his finding to the Royal Agricultural Society that soils were able to remove ammonia from aqueous solution. Maclean¹ and Kerr² reported that soil acidity and ion exchange properties of soils were due to clay content. The absorption of cations by a clay mineral does not involve any structural change in the mineral. In the process one cation is taken up from the solution and another is released in the solution. Exchange is taken place between two types of cations, so the process is known as cation exchange process. Total amount of cation exchange taken place in 100 g of clay is known as cation exchange capacity (c.e.c.) of the clay. It is very usual for a neutral clay to absorb several cations, common ones are H⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, and Al³⁺. It is customary to distinguish between clays in which one cation is predominantly or exclusively absorbed. Thus a sodium clay is one in which the absorbed cation is sodium and it may be represented as (clay) Na and the exchange reaction between two cations may be expressed as (clay) Na + NH₄(OH) = (clay) NH₄+ NaOH. C.e.c. is an important physical property and it has got relation with various important physical characteristics of the clay, e.g., plasticity, shrinkage, drying property, viscosity of a clay slip, etc., particularly when the clay is in the water medium. So c.e.c. value provides useful information to the ceramist as to the nature of the minerals in a clay.

With a view to get adequate knowledge of working properties of some East Pakistani clays, c.e.c. of Bejaipur clay, Mirpur clays (Red and Black) and Dacca river silt were determined.

Experimental

Clay was beneficiated by the method described by M. Khuda et al.⁴ and dried at 100°C and powdered to 200 mesh. The direct method⁶ was used. Ammonium clay was prepared by treating clay with ammonium salt solution. Mattson⁷ used ammonium chloride solution for leaching soils, the washed soil being used for determination of the total cation exchange capacity. Pierre and Scarseth⁸ also used ammonium chloride for the same purpose. Ten g of beneficiated clay was taken in a 500 ml conical flask and to this 300 ml 1.0N ammonium chloride solution was added. The contents was shaken for nearly five hours in a shaking machine and then was allowed sufficient time to settle clay particles. The solid phase was separated by decantation and clay was treated again with 200 ml ammonium chloride solution. Four times such treatments were carried out with ammonium chloride solution to ensure complete replacement of exchangeable ions of clay. After the last treatment contents was collected in a known volume of standard sulphuric acid. The liberated ammonia was estimated by a back titration with a standard solution of alkali. The experimental procedure using ammonium acetate for making ammonium clay is the same as the one described.

In the second set of experiments hydrogen clay was made by treating the sample with N/10 hydrochloric acid. The contents was shaken for five
QUANTITATIVE ESTIMATION OF KAOLINITE IN CLAYS 
BY DIFFERENTIAL THERMAL ANALYSIS

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A quantitative method of estimating the kaolinite content in clays by differential thermal analysis, using magnesium hydroxide as an internal standard, is presented. The effects of variations due to particle size, and impurities such as quartz, iron oxides, hydrated alumina minerals and organic material are discussed.

Several authors have used quantitative differential thermal analysis as a rapid, inexpensive and accurate method for the determination of the amount of a particular mineral in a mixture. The kaolinite content of a clay sample has been estimated from the area of the endothermic peak at 575°C. Speil1 and Kerr and Kulp2 showed on theoretical grounds that the area of any particular peak on a DTA curve is proportional to the heat evolved by the total mass of the reacting substance. However, Speil, Berkelhammer, Pask and Davies3 found variations of some 30% in the heats of transformation of kaolinite from various origins. Grim4 has shown that variations in size and degree of crystallinity of particles of kaolinite are reflected in variations in the intensities of thermal reactions of the mineral. Carthew5 has also studied the effects of the degree of crystallinity and particle size distribution of kaolinite on the endothermic peak of the DTA curve. He has shown that the ratio of the area to the width at half the amplitude of the endothermic peak increases with the “slope ratio”, and his empirical relationship provides a method of quantitatively estimating the proportions of kaolinite of various particle sizes and degree of crystallinity.

In the present paper, authors suggest a simple method of estimating the amount of kaolinite present in clays by using magnesium hydroxide as an internal standard. A small amount of ignited alumina (inert) is also added to improve the sharpness of the peak. The effects of particle size, and the interference due to the presence of quartz, iron oxides, hydrated alumina minerals and organic materials are also studied.

Experimental

Equipment and Procedure.—Aliquots of about 0.3 g of material (sample and alumina) were placed in the three holes (one containing sample and two containing alumina) of a stainless steel crucible, and subjected to a uniform rise in temperature (10°C/min) in a vertical furnace having nichrome wires as the heating element. The furnace temperature is controlled manually by a variable transformer, and chromel-alumel thermocouples (25 gauge) are used for measuring the temperatures. The differential temperature is recorded on an automatic Cambridge recorder, having a scale extending from +1 mv to−1 mv. The recorder, driven by an electrical clock marked every twenty seconds on a chart 95 mm wide with a maximum duration of 125 min.

Preparation of the Mixture.—A.R. grade magnesium oxide was soaked in water overnight, then dried in an oven at 140°C. The dried material was powdered to −100 mesh and kept in an air-tight bottle.

A.R. grade alumina was ignited to 1000°C. The material was then cooled and powdered to −100 mesh.

BDH kaolin was used for the construction of the working curve. A series of mixtures of kaolinite, magnesium hydroxide and alumina were prepared and analyzed thermally. The various DTA curves are given in Fig. 1, and the results are summarized in Table 1. The ratio of the area of the endothermic peak of kaolinite to the area of the peak of magnesium hydroxide is seen to be closely proportional to the concentration of kaolinite (Fig. 2).

The optimum amount of internal standard was worked out to be 10 percent by weight of the whole mixture. The endothermic peak of magnesium hydroxide at this concentration was observed to be broad, but the addition of 10% inert alumina was found to improve the sharpness of the peak. Thus, each unknown sample is diluted by a factor of (100−20)/100, and the actual amount of kaolinite must be obtained by multiplying the amount indicated from the graph (Fig. 2) by a factor of 100/80=1.25.

Reproducibility and Tests on Known Samples.—Measurements of the heat effects are influenced
SOME OBSERVATION ON THE MINERALOGY AND CHEMISTRY OF THE PLEISTOCENE ALLUVIUM FROM MIRPURE AREA, DACCA

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A preliminary study of the Pleistocene alluvium from Mirpure area, Dacca has been carried out with respect to its texture, mineralogy and chemistry. The clay falls in the category of “loam” with none of the sand, silt and clay fractions generally exceeding 50%. Chemically the clay may be termed as sublaticrite markedly enriched in alumina and iron oxide and deficient in lime and magnesia. The mineralogical study of the coarse fraction separated from the clay indicates the presence of, besides other light minerals, clear grains of labradorite and bytownite. Heavy minerals consists of sillimanite, zircon, kyanite, topaz, tourmaline, staurolite and rutile in order of decreasing abundance. The suite of heavy minerals suggests a mixed percentage.

On the basis of mineralogical study it is suggested that the ‘old alluvium’ of Mirpure has been largely derived from igneous and metamorphic source rocks. Further, it is suggested that the sediments have been deposited under subaerial condition most probably fluviatile.

The alluvial flat in East Pakistan is generally separated into two distinct physiographic units. One is the so called ‘old alluvium’ and the other is the new alluvium deposited by the intricate river system of East Pakistan during the Recent. The ‘old alluvium’ stands out prominently as physiographically elevated unit and is supposed to have been deposited during the Pleistocene epoch the material of which has been deprived from the north.

Besides several smaller outcrops, there are two large tracts predominantly covered by ‘old alluvium’—Barind and the Modhupur jungle Fig. 1. The Barind covers an area of 2500 sq miles and lies between Ganges and Barhamputra forming the northwestern part of East Pakistan. The Modhupur tract covers an area of 1600 sq miles between Meghna and Barhamputra rivers extending from Dacca in the south to Jamalpur in the Mymensingh district in the north. The tract stretches for about 70 miles along north-south while its extent along east-west is only about 35 miles. Its present elevated position attaining a maximum height of 100’ above sea-level along the western margin with respect to the surrounding alluvial flat of the Recent is considered to be due to ‘enechelon faulting’. The Modhupur jungle gradually slopes down towards east to be overlapped by the alluvium of the Recent.

Paucity of literature on the subject indicates that the ‘old alluvium in general has been given very little attention by geologists. Such inadequate published literature as exist point towards the necessity of a more detailed investigation than has hitherto been carried out.

The present preliminary investigation has therefore been undertaken to determine quantitatively

MAP SHOWING THE DISTRIBUTION OF ‘OLD ALLUVIUM’ IN EAST PAKISTAN, AND THE AREA STUDIED
MICRO-DIFFERENTIAL THERMAL ANALYSIS TECHNIQUE WITH THE HOT-STAGE MICROSCOPE

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(Received May 10, 1969)

The construction and operation of a micro-differential thermal analyser in corporation with the hot-stage microscope are described. Based upon the use of two opposed, viewable thermocouple microfurnaces, the instrument provides a sensitive means of detecting heat effects with accompanying reactions which may occur when small quantities (< 1 mg) of materials are rapidly quenched or undergoing programmed temperature change.

The differential thermal analysis technique is widely used as means of detecting thermal effects associated with chemical and structural changes in materials. For most application every analyser so far described is based on a conventional furnace which is used to heat or cool a suitable container for both specimen and thermally inert substance, called the standard and when a reaction temperature is reached, the accompanying heat change in the material is registered as a temperature difference between the opposed thermocouples whose measuring junctions are embedded in the two materials. The majority of such instruments require microscopic quantities of materials and the total thermal capacities of these assemblies limit the rate of temperature change that can be imposed. It is unusual for heating or cooling rates higher than 20°C/min to be used; a generally accepted standard rate being 10°C/min.

There has recently been some development of micro-differential thermal analysis apparatus in order to improve the temperature definition by the removal of thermal gradients between the reacting materials and the thermocouples. A successful design is that of Maziers, who achieved both sensitivity and higher resolution. An arrangement that permits visual observation during thermal analysis has also been described by Hogan and Gordon. Mercer and Miller and M. A. Rochelle have made considerable advances by combining high temperature microscopy with thermal analysis and by modifying the hot-stage microscope developed by Welch. These modifications provided a means for continuously monitoring and recording the cooling curves of microscopic quantities of materials, which are supported in the viewable thermocouple microfurnace of the hot-stage microscope. In this form the apparatus has been used for high temperature phase studies in oxides and mineral systems, where emphasis has been put on determining both equilibrium and nonequilibrium behaviour in terms of variable thermal history.

The detail of the high speed thermal analysis has been published. The introduction of two channel heating and oscilloscope monitoring of cooling curves extended the application of the technique to include microscopic thermal analysis between two pre-selected temperatures. The present high temperature microscope was also successfully used to study the effects of varying the cooling rate on the crystallization of beryllia containing melts. These experiments were successful because beryl melts display large exothermic heat effects during rapid cooling and can be observed on curve of temperature versus time. But titanium containing slag exhibited no such large exothermic effects on the cooling curve although they did crystallise. An obvious refinement, therefore, would be the conversion of the high temperature microscope to differential thermal analysis with corresponding enhanced sensitivity. In order to incorporate the principle of differential thermal analysis into the high temperature microscope the following requirements had to be met.

(i) Retention of the facility for continuously observing the specimen.

(ii) The ability to control separately the upper and lower temperature of both thermocouples. This is necessary to annul temperature differences that would result if there is unequal thermal capacity; for example from difference in size and loading.

(iii) Simultaneous heating of sample and the standard and the measurement of sample temperature and differential temperature between the sample junction and inert junction.
MINERALOGICAL STUDIES ON SOME HIGH ALUMINA BAUXITIC CLAYS FROM SALT RANGE AREA

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X-Ray, D.T.A., P.C.E. and other data are presented for three selected high alumina bauxitic clays from salt range area. A correlation between X-Ray data of the raw bauxites and the other properties obtained revealed that the materials contain a very high proportion of boehmite (70 to 75%). After calcination they contain Al₂O₃ 70 to 80%. These bauxites may, therefore, be used for making mullite and other high alumina refractories to be used in high temperature furnaces and kilns for chemical glass, Cement, ceramic, iron and steel and other metallurgical industries.

The term “Bauxite” is usually applied to aluminium ores generally believed to consist of a mixture, in different proportions, of the trihydrate (gibbsite) and the monohydrates (Boehmite, diaspor, etc.) with certain impurities. The impurities are principally the iron minerals hematite, various hydrated ferric oxides, siderite, etc., Silica is usually found in the combined form of kaolinite and halloysite, and titanium present possibly as rutile, ilmenite or leucoxene. Harder indicates that all of the boehmite and diaspor deposits are of an early age, while all the more recent deposits are of the trihydrate, gibbsite type. It seems, therefore, that gibbsite forms first during the laterization of aluminium-silicates and that ageing, pressure and possibly heat, change the gibbsite to boehmite and eventually to diaspor.

Previously some information on the mineralogical nature and the ceramic properties of a high alumina clay has been reported. The objective of the present study was to examine the three samples of Bauxitic clays quantitatively with respect to initial mineralogy through chemical analysis, Differential Analysis and finally through X-Ray studies and to correlate the data obtained and thus to establish the economic interest in these high alumina bauxitic clays by contributing information, providing a better understanding of their high temperature application in Industry. Three high alumina bauxitic clay samples were collected from the outcrops of three different beds which are 3-4 miles away from each other. The general strike of the bauxitic beds is more or less East-West with a dip of about 30 to 35°, and lie at an altitude of about 2000 to 2500 feet above sea level, approachable from Katha, Pail and Sultan Mehti etc. The deposits start from near village Kutha which is located some 18 miles north of Khushab Tehsil in Sargodha Dist. High alumina bauxitic clays seem to be scattered over most of the Central Salt Range area including the Sakser hills. Various veins having upto 30 feet thickness and over 10 miles length have been noticed and the probable reserves seem to be of several million tons. The predominant colour of the bauxites is cream, buff and white.

Experimental

Chemical analyses of the three samples as given in Table-I have been made and their fusion temperatures have been measured to determine the maximum useful temperature to which they could be fired, and hence their suitability as refractory materials. The calculated mineralogical compositions of the clays are given in Table 2.

The procedure, method, and instrument used for the differential thermal analyses have been discussed previously. The clays were perfectly ground, passed through a 100 mesh sieve, dried at 110°C. They were then put into the apparatus for heat application, and the minerals present in this have been identified by the obtained endothermic and exothermic peaks. The differential thermal curves of the three samples are presented in Fig. 1.

X-Ray analyses have been made using wide range Norelco diffractometer and employing a

<table>
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<th>L/I %</th>
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<th>Al₂O₃ %</th>
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<th>TiO₂ %</th>
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STUDIES ON PREPARATION OF SOLUBLE FLUORIDES DIRECTLY FROM CALCIUM FLUORIDE

Part I. From Pure Calcium Fluoride

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The reaction between calcium fluoride and various alkali salts in the aqueous medium at atmospheric and high pressure was studied. No reaction is observed at atmospheric pressure. Reaction at 50–125 lb/in$^2$ pressure was observed only with alkali carbonates suggesting the usefulness of this method for industrial utilization for the preparation of alkali fluorides. Quantitative conversion on fusion of calcium fluoride and alkali carbonates was also observed.

Fluorine and its compounds find an important place in industrial chemistry. For detailed information reference may be made to Bartley.\textsuperscript{1,2,3}

The two sources of fluorine are the mineral fluorspar in which fluorine is present as calcium fluoride, and rock phosphate from which it is recovered as a by-product. The rock phosphate being used in Pakistani industry is of foreign origin containing an average of 3\% fluorine.\textsuperscript{4,5} However no effort is presently being made to recover the valuable byproduct. Flurospar has been reported to occur in Koh-i-Maran Range in Kalat District and in Hazara District.\textsuperscript{6}

The starting point for fluorine chemicals is the manufacture of hydrofluoric acid according to the reaction:

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}.$$  

Acid grade fluorspar required for this purpose must contain a minimum of 95\% CaF$_2$.\textsuperscript{7}

Safdar and his co-workers\textsuperscript{8} attempted to employ this reaction \textit{in situ} for the frosting of glass. They noted that when fluor spar was used the reaction was too slow to be of any direct practical utility. In view of the considerable importance of soluble inorganic fluorides it was considered desirable to study the feasibility of by-passing the preparation of hydrofluoric acid. The present communication describes the investigation made with pure calcium fluoride.

Experimental

A.R. calcium fluoride and other chemicals were used.

Fusion experiments were performed in an electric muffle furnace in iron crucibles. Aqueous reactions were carried out at atmospheric pressure at 90$^\circ$C.

A gas-heated steel autoclave of working pressure up to 125 lb/in$^2$ was used for pressure experiments. The time of autoclaving taken into account was counted from the time the particular pressure was achieved.

The fluoride rendered soluble was estimated gravimetrically by precipitating fluoride as lead chlorofluoride\textsuperscript{9} between the limit 0.01 to 0.10 g.

Discussion

Fusion Experiments.—Fusion of calcium fluoride was carried out with sodium, potassium and lithium carbonates at temperatures ranging from 900 to 1200$^\circ$C, keeping the carbonate content constant and varying the calcium fluoride content. The results are shown in Figs. 1, 2 and 3 which show that in each case almost the theoretically calculated molar yields are obtained. The maximum conversion to alkali fluorides was obtained at 1200$^\circ$C. At higher temperatures no further increase was evident which could possibly be due to the volatilization of alkalies.

In terms of percentage molar yields the maximum amounts to 93.87 for lithium, 94.97 for sodium and 95.58 for potassium fluoride. It will thus be seen that although a definite trend according to the alkali ion present in the order K $>$ Na $>$ Li is observed, the effect of the alkali metal ion is not appreciable. KF, NaF and LiF have an electronegativity of 4.8, 4.9 and 5.0 respectively and the yields, however, follow the reverse trend.