

TABLE I
Fragmentation data of 4-(Benzalamino) antipyrines.

Compound Ar	Ions m/e (%)					
	a	b	c	d	e	M ⁺
1a C ₆ H ₅	56 (100)	188 (23)	121 (25)	199 (18)	182 (11)	291 (55)
1b 2-FC ₆ H ₄	56 (100)	188 (29)	121 (29)	217 (16)	200 (9)	209 (51)
1c 2-ClC ₆ H ₄	56 (100)	188 (31)	121 (40)	233 (14)	216 (6)	325 (35)
1d 2-BrC ₆ H ₄	56 (100)	188 (33)	121 (31)	277 (13)	260 (5)	369 (26)
1e 4-HO-C ₆ H ₄	56 (100)	188 (13)	121 (20)	215 (14)	198 (11)	307 (54)
1f 2-HO-C ₆ H ₄	56 (100)	188 (32)	121 (32)	215 (25)	198 (3)	307 (70)
1g 2-CH ₃ O-C ₆ H ₄	56 (100)	188 (5)	127 (7)	229 (5)	212 (5)	321 (18)

to assign a straight forward mechanistic pathway for the formation of this ion. It is clear that extensive skeletal rearrangement has taken place leading to the formation of the above ion. The ion has only a low abundance (ion e).

The chloro and bromo derivatives give M-X ions also of moderate intensity.

Thus in comparison with the mass spectra of antipyrine² the present compounds show interesting fragmentation modes obviously brought about by the introduction of the arylidene amino moiety at the 4th position of the antipyrine ring. Ring fragmentation involving the loss of CO or loss of Ph NCO is not observed.

The mass spectra were taken Varian MAT-CH7 at the inlet temperature 195°C. Direct inlet system was used to introduce the compounds. The m/e values and the percentage abundance of selected ions are given in table I. The compounds were obtained by a procedure reported earlier⁵. Satisfactory elemental analysis data were obtained for all the compounds. The purity was ascertained by thin layer chromatography using silica gel (benzene).

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SYNTHESIS OF 2,6-DIARYL-4H-1,3,4-OXADIAZINES AS ANTI-BACTERIAL AGENTS

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THE synthesis of many substituted and fused 1,3,4-oxadiazines as monamine oxidase inhibitors have been reported earlier¹⁻⁵. 5,6-dihydro-4H-1,3,4-oxadiazines were synthesized from certain 2-(β-hydroxyalkyl) acid hydrazides⁶. Reactions of certain acid hydrazides with quinones gave fused oxadiazine systems⁷. It is of interest to extend this reaction with phenacyl chloride to synthesise oxadiazines and to screen them for antibacterial activity.

Phenacyl chloride (I) was made to react with acid hydrazides (IIa-f) to get 1-N-phenacyl acid hydrazides (IIIa-f). For the subsequent cyclisation acetic acid, acetic acid-sulphuric acid and acetic acid-phosphoric acid were used.

1-N-Phenacyl anisic acid hydrazide (IIIc):

It was prepared in two ways.

(1) A mixture of phenacyl chloride (0.0064 mol), anisic acid hydrazide (0.0064 mol) and 2 or 3 drops of piperidine in alcohol (30 ml) was refluxed for 6 hr and poured into crushed ice with constant stirring. It was kept aside for a few minutes and the product separated was filtered, washed with cold water, dried and recrystallized.

(2) To a solution of phenacyl chloride (0.1 mol) in acetic acid (20 ml) *p*-anisic acid hydrazide (0.1 mol) in acetic acid (20 ml), was added. The mixture was heated under reflux for 3-4 hr. The reaction mixture was cooled and poured into ice with constant stirring. The resultant solid was filtered, washed with water, dried and purified by crystallization. Similarly other

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TABLE I
1-N-phenacyl acid hydrazides (III).

No.	R	m.p. (°C)	IR	cm ⁻¹	δ max
a	-H	90	3400,	3220,	1710, 1680
b	-CH ₃	100	3400,	3210,	1720, 1700
c	-OCH ₃	80	3400,	3220,	1720, 1700
d	-OH	120	3390,	3220,	1710, 1680
e	-NO ₂	130	3400,	3190,	1690, 1670
f	-Cl	155	3400,	3210,	1730, 1680

Compounds III (a-f) were crystallized from benzene. Analytical data agreed with the calculated values within the limits of experimental error.

substituted 1-N-phenacyl acid hydrazides were prepared and are recorded in table 1.

2-Anisyl-6-phenyl-4H-1,3,4-oxadiazine (IVc):

Polyphosphoric acid was prepared by stirring a mixture of P₂O₅ (12 g) and phosphoric acid (6 ml) at 100-110°C for an hr. To this was added 1-N-phenacyl anisic acid hydrazide (1 g) in acetic acid (20 ml) and the stirring was continued for a period of 6-8 hr at 140°C. Subsequently the reaction product was cooled and decomposed with ice cold water. The solid that separated was filtered and washed with aq. NaHCO₃ (5%) and water. It was dried and recrystallized.

Similarly compounds IVa, b and d-f were prepared and are recorded in table 2.

The results were confirmed by analytical, IR, NMR and Mass spectral data. Melting points were determined in open capillaries and are uncorrected. TLC

TABLE 2
2,6-diaryl-4(H)-1,3,4-oxadiazines (IV).

No	R	m p. (°C)	IR	cm ⁻¹	δ max
a	H	100	3400,	1600,	1280
b	CH ₃	115	3410,	1595,	1260
c	OCH ₃	110	3400,	1630,	1250
d	OH	130	3420,	1600,	1255
e	NO ₂	150	3400,	1590,	1260
f	Cl	160	3400,	1600,	1265

Compound IV(a-c) were crystallised from chloroform; IV(d and f) from methanol and IVe from acetic acid. Analytical data agreed with the calculated values within the limits of experimental error.

was performed on silica gel plates using benzene chloroform (2:1) as solvents.

In the reaction between I and IIa-f the formation of 1-N-phenacyl acid hydrazides (IIIa-f) can be explained by the observation that the more basic -NH₂ group in II replaces the ω-halogen of (I) giving rise to III as observed by Baker⁸ in reaction of phenacyl chlorides with amines. 1-N-phenacyl acid hydrazides do not give FeCl₃ test, halogen test and carbylamine test confirming their structures as IIIa-f. Cyclodehydration of IIIa-f giving rise to oxadiazines was prominent with acetic acid-phosphoric acid. The reaction was partial with acetic acid-sulphuric acid. A moderate reaction was noticed when R = H, but it proceeded faster when R = -CH₃, -OH or -OCH₃. The reaction is slowed down by the presence of electron withdrawing nitro-group.

The results of the present investigation are based on the following data.

1-N-phenacyl anisic acid hydrazide (IIIc):

Anal: Calc: For C₁₆H₁₆N₂O₃: C, 67.60; H, 5.63; N, 9.85%

Found: C, 67.65; H, 5.66; N, 9.82%

IR 3220 cm⁻¹ (-NH amide), ~3400 cm⁻¹ (-NH), ~1720 cm⁻¹ (-C=O) 1700 cm⁻¹ (-C=O amide).

PMR (CDCl₃/DMSO-d₆): 3.8 δ (s, 3H, -OCH₃); 3.9 δ (s, 2H, -CH₂-); 5.5 δ broad peak (-NH proton exchangeable with D₂O); 5.9 δ broad (H, -NH amide exchangeable with D₂O) aromatic protons of phenacyl moiety are observed at 6.8 δ (2H); 7.2 δ (2H) and 7.75 δ (5H) phenyl protons of acid hydrazide.

Mass spectrum: M⁺ (molecular ion) m/z 284 (5%) and base peak m/z 135 (100%, p-H₃CO-C₆H₄-C=O⁺).

2-anisyl-6-phenyl-4H-1,3,4-oxadiazine (IVc):

Anal: Calc: For C₁₆H₁₄N₂O₂: C, 72.18; H, 5.26; N, 10.52%.

Found: C, 72.20; H, 5.23; N, 10.55%

IR ~3300 cm⁻¹ ~3400 cm⁻¹ (-NH), ~1630 cm⁻¹ (-O-C=N-) and ~1250 cm⁻¹ (=C-O-C=).

PMR (CDCl₃): 3.8 δ (s, 3H, -OCH₃); 5.5 δ (s, vinylic proton); 6.5-8.1 δ (m, 9H, phenyl protons and the -NH oxadiazine system).

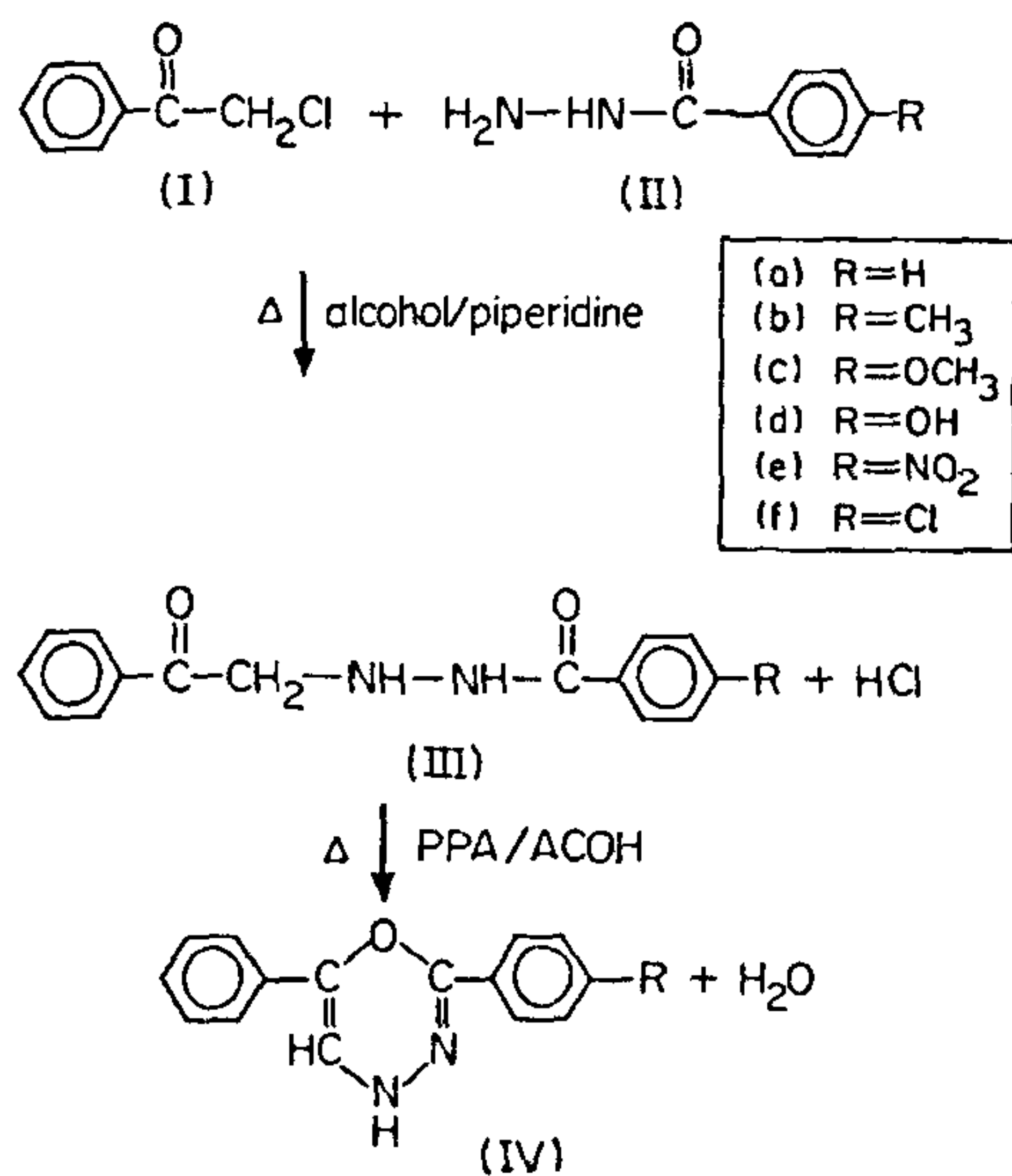
Mass spectrum: M⁺ (molecular ion) at m/z 266 (10%) and base peak m/z 44 (100% H₂N=C=O⁺).

Biological screening

Antibacterial Activity: Compounds IVa-f were screened for their antibacterial activity using the method of Vincent and Vincent⁹. The gram +ve and

TABLE 3
Effect of 2,6-diaryl-4H-1, 3,4-oxadiazines (IVa-f) on four bacteria.

Compound	Concentration in ppm	Diameter of zone of inhibition (mm)			
		<i>B. pumilus</i> (+)	<i>B. subtilis</i> (+)	<i>P. ovalis</i> (-)	<i>P. vulgaris</i> (-)
IVa	100	7	-	-	-
	300	9	7	-	-
	1000	12	8	-	-
IVb	100	9	3	-	-
	300	10	5	-	-
	1000	13	6	-	-
IVc	100	8	-	-	-
	300	11	4.5	-	-
	1000	12	6.5	-	-
IVd	100	8	-	-	-
	300	12	-	-	-
	1000	13	-	-	-
IVe	100	8.4	-	-	-
	300	10	-	-	-
	1000	12	-	-	-
IVf	100	6	-	-	-
	300	7.5	-	-	-
	1000	9	-	-	-



Scheme - 1

gram - ve bacteria employed for the tests were *Bacillus subtilis*, *Bacillus pumilus*, *Pseudomonas ovalis* and *Proteus vulgaris*.

Compounds IVa-f were ineffective against *P. ovalis* and *P. vulgaris* which are gram negative bacteria. They were, however, inhibitory towards gram positive bacteria vis., *B. subtilis* and *B. pumilus*. The results are presented in table 3.

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LOWER JURASSIC FORAMINIFERA FROM THE CHERT-PHOSPHORITE MEMBER OF THE TAL FORMATION, GARHWAL LESSER HIMALAYA AND THE AGE OF KROL BELT SEDIMENTS

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THIS record of the Lower Jurassic foraminifera, annelids and seemingly reworked Cambro-Ordovician conodonts from the lowermost unit of the Tal Formation is very significant in fixing more precisely the age of the largely unfossiliferous sediments of the Lesser Himalayan Krol-belt in view of the recent claims regarding their age-Cambro-Ordovician for some¹, late Precambrian² for others. The present fauna has been recovered from fairly hard, calcareous, black shale with chert and phosphorite of the Lower Tal Formation from the phosphate mine, Adit No. 1 (at 825m level) of the PPCL at Maldeota near Dehradun, UP. A total of six samples collected at an interval of roughly 30 cm each were acidized and, on careful examination and comparison 25 species of foraminifera were identified, of which 7 (herein mentioned as sp. indet.) seem to be new (table 1, Figures 1-30).

This is the first record of such a prolific assemblage of smaller benthonic foraminifera from this sequence, besides some doubtful foraminiferal tests observed earlier in thin sections^{3,4}. The faunal association, though poor in typical Jurassic Lagenids, is in general suggestive of the Lias age for the Chert-Phosphorite sequence of the Lower Tal Formation. Some foraminiferal species are characteristic forms starting from Lias only, while a few other, belonging to genera *Ammovertellina*, *Clavulina* and *Textulariella*, generally appearing later in the geological column, also occur in this material but their occurrence has been similarly reported earlier from Lias of elsewhere in the world (table 1). It has been observed that the tests of these foraminifera are brownish to black in colour and exhibit some amount of phosphatization. This condi-

tion was probably responsible for their rich yield even after conventional acetic acid treatment normally given to carbonates for conodont recovery. Also, more calcareous and less phosphatic bands in this Chert-Phosphorite sequence are richer in foraminiferal content while conodonts predominate in the less calcareous and more phosphatic bands. Further, the foraminiferal fauna with a few annelids is indicative of shallow water marine environment under reducing conditions which are deduced from phosphatised tests of foraminifera, pyrite nodules and gypsum grains. It may be mentioned here that all forms recovered from the same sequence were earlier identified as Late Cretaceous annelids⁵.

A large number of fragmentary, abraded and simple, hollow cone-type reworked conodonts of Cambro-Ordovician (Tremadocian) age, earlier described by Azmi *et al.*¹, are also associated with the present material. Rich elements belonging to at least 11 different taxa of conodonts in this material point to the Cambro-Ordovician¹ age but their association with even more abundant and largely Liassic foraminifera in the same material is doubtless enigmatic. However, this anomaly can be explained by visualising a derived conodont plexus possibly from the carbonates of the Mandhali Formation belonging to the Jaunsar Group of late Precambrian-early Paleozoic age which were eroded off prior to the deposition of the Blaini-Krol-Tal sequence⁶⁻⁸.

In order to confirm the true biological affinity of these organisms, some of which have been earlier mistaken for annelids, a number of thin sections were made to study the internal structure of their tests (figures 28-30). These sections have invariably presented a camerate structure thus demonstrating the presence of multilocular organization of a test rather than an open, simple tube characteristic of an annelid.

Sedimentological observations along the contact of Tal Quartzite with the uppermost Tal Limestone at Singtali, Medi Gad and Dugadda in parts of neighbouring Lansdowne Hills reveal a transitional and conformable change with the following characters: (i) presence of abraded overgrowth on detrital quartz grains, glauconite grains and isolated fossil fragments in both the formations, (ii) intermittent carbonate cement towards the upper contact of the Tal Quartzite, (iii) presence of at least three, largely unfossiliferous, quartzite horizons within the Tal Limestone having similar lithology as the underlying Tal Quartzite in Singtali and Dugadda sections, (iv) almost total absence of oolite growth in quartzite bands within the Tal Limestone as well as in the Tal Quartzite.

Taking the contact of the Tal Quartzite with the overlying limestone as conformable, it is evident that the arenites of the Tal Group belong to Cretaceous