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1-Aroyl-2-[3-*n*-butoxy-5-oxo-4-phenyl-2(5H)-furylidene) phenyl acetyl hydrazines(III) were the products when the reaction was conducted in *n*-butanol due to the etherification of enolic hydroxyl in the presence of a base. All the products were adequately characterized by IR, NMR and high resolution mass spectral data. A few of the new derivatives showed promising activity against some bacterial strains.

Pulvinic dilactone reacted with substituted acid hydrazides in boiling dry xylene containing a small amount of pyridine to form 1-aryol-2-[(3-hydroxy-5-oxo-4-phenyl-2(5H)-furylidene)-phenyl-acetyl] hydrazines(II). IR spectra of all the products displayed two strong carbonyl absorptions, at 1730 and 1650 cm^{-1} for lactone and amide group respectively. The 200 MHz PMR of II_a confirmed this by showing two complex multiplets at 7.3–7.7 and 7.9–8.1 for aromatic hydrogens and two D₂O washable signals at 10.6 and 11 respectively for amide and enolic hydroxyl protons.

In the mass spectrum, molecular ion did not appear owing to weak amide linkage in II_a. On the other hand, the spectrum presents all the signals due to pulvinic dilactone and benzoic hydrazide due to reversal of the reaction. The prominent signals are at *m/z* 290, 234, 178, 117, 89 and 63 for pulvinic dilactone¹, 136 and 105 due to benzoic hydrazide and at 264 for pulvinone.

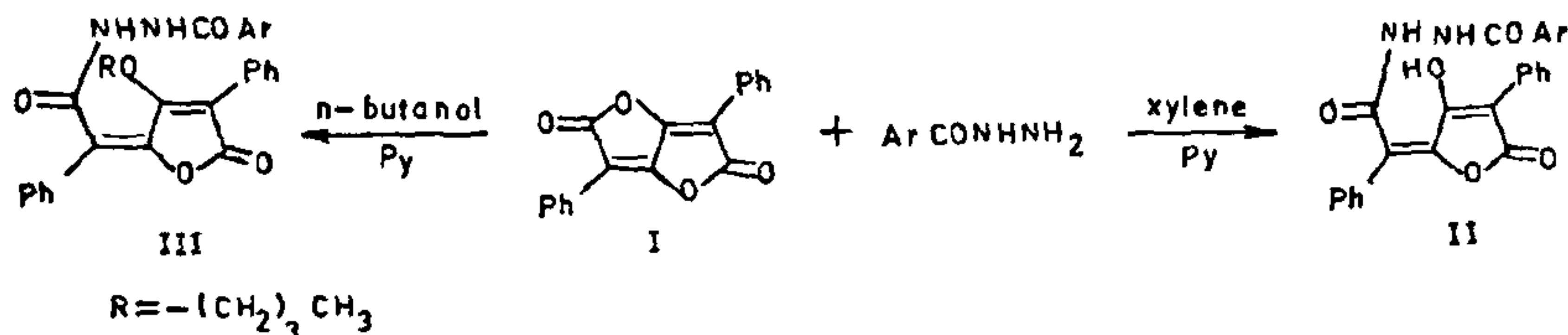
In *n*-butanol, pulvinic dilactone condensed with aroyl hydrazide in the presence of a few drops of pyridine to give 1-aryol-[3-*n*-butoxy-5-oxo-4-phenyl-2(5H) furylidene phenyl acetyl] hydrazines(III) (scheme 1). In acidic medium the enolic hydroxyl underwent etherification with the solvent. In addition to lactone and amide carbonyls appearing at 1710 and 1640, aliphatic vinyl ether stretchings are observed at 1320 and 1040. Aliphatic signals at 0.8, 1.4 and 4.1 for *n*-butoxy group and a neat singlet at 2.5 for aromatic methyl function presented a strong evidence to the structure of III_b. A complex

CHEMISTRY OF LICHEN PRODUCTS: PART VII: SOME NEW AMIDE DERIVATIVES FROM THE REACTION OF ACID HYDRAZIDES WITH PULVINIC DILACTONE

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PULVINIC dilactone (I) reacts with acid hydrazides in dry xylene containing catalytic amount of dry pyridine to afford 1-aryol-2-[(3-hydroxy-5-oxo-4-phenyl-2(5H)-furylidene)-phenyl-acetyl] hydrazines(II).



Scheme 1.

multiplet between 7.3 and 7.8 for aromatic protons and a D₂O exchangeable singlet at 9.2 due to amide hydrogens are also observed.

Unlike natural and synthetic pulvinamides, III_b did not undergo reversal of the reaction owing to the presence of *n*-butoxy group. A free enolic hydroxyl would have resulted in the appearance of a strong signal at *m/z* 290 due to pulvinic dilactone. The M⁺ signal for the compound did not appear. Based on elemental composition with minimum deviation offered in high resolution mass spectrum, the ions responsible for the signals have been formulated (chart 1).

Antibacterial activity

The activity results of a few selected compounds tested against *Bacillus polymixa* (A), *Bacillus pumilis* (B), *Streptococcus albus* (C), *Proteus vulgaris* (D), *Pseudomonas ovalis* (E) and *Acetobacter aerogen* (F) by cup plate method² are presented in table 1.

Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded in nujol and PMR in DMSO-d₆.

Table 1 Characterization and activity data of II and III[†]

Compd.†	Ar	m.p. (°C) yield (%)	Molecular formula	% Composition found (Calcd.)			Antibacterial activity* Zone of inhibition**					
				C	H	N	A	B	C	D	E	F
II _a	Phenyl	108 (70)	C ₂₅ H ₁₈ O ₅ N ₂	69.5 (70.4)	4.0 (4.2)	6.3 (6.5)	12	14	12	12	14	12
II _b	<i>p</i> -Anisyl	112 (50)	C ₂₆ H ₂₀ O ₆ N ₂	69.5 (68.4)	4.2 (4.3)	5.8 (6.1)	12	12	10	12	10	12
II _c	<i>p</i> -Cl-Phenyl	126 (58)	C ₂₅ H ₁₇ O ₅ N ₂ Cl	64.5 (65.2)	3.5 (3.6)	5.7 (6.0)	18	16	18	18	16	18
II _d	Phenoxymethyl	92 (62)	C ₂₆ H ₂₀ O ₆ N ₂	68.5 (68.4)	4.2 (4.3)	6.2 (6.1)	—	—	—	—	—	—
II _e	<i>p</i> -NO ₂ -Phenyl	134 (52)	C ₂₅ H ₁₇ O ₇ N ₃	63.2 (63.7)	3.5 (3.6)	8.3 (8.9)	20	18	20	20	18	20
II _f	Benzyl	106 (60)	C ₂₆ H ₂₀ O ₅ N ₂	70.2 (60.9)	4.3 (4.5)	6.2 (6.3)	14	16	12	12	12	14
II _g	α -Naphthyl methyl	127 (63)	C ₃₀ H ₂₂ O ₅ N ₂	72.5 (73.4)	4.2 (4.4)	5.5 (5.7)	—	—	—	—	—	—
II _h	Nicotinyl	136 (55)	C ₂₄ H ₁₇ O ₅ N ₃	67.3 (67.4)	3.8 (3.9)	9.7 (9.8)	16	16	18	14	18	18
II _i	Isonicotinyl	132 (50)	C ₂₄ H ₁₇ O ₅ N ₃	66.8 (67.4)	3.6 (3.9)	9.5 (9.8)	—	—	—	—	—	—
II _j	<i>p</i> -Cl-Phenyl	122 (50)	C ₂₄ H ₁₇ O ₅ N ₂ Cl	63.8 (65.1)	3.5 (3.6)	5.8 (6.0)	14	12	14	14	16	14
II _k	3,5-di-NO ₂ -Phenyl	232 (62)	C ₂₅ H ₁₆ O ₉ N ₄	58.1 (57.5)	3.0 (3.1)	9.9 (10.8)	20	20	20	18	18	20
II _l	<i>p</i> -OH-Phenyl	98 (45)	C ₂₅ H ₁₈ O ₆ N ₂	67.5 (67.8)	3.8 (4.0)	5.8 (6.3)	—	—	—	—	—	—
II _m	<i>o</i> -OH-Phenyl	242 (75)	C ₂₅ H ₁₈ O ₆ N ₂	67.4 (67.8)	4.0 (4.0)	6.2 (6.3)	—	—	—	—	—	—
III _a	Phenyl	110 (68)	C ₂₉ H ₂₆ O ₅ N ₂	71.5 (72.1)	5.0 (5.3)	5.6 (5.8)	14	12	10	10	12	14
III _b	<i>p</i> -Tolyl	162 (57)	C ₃₀ H ₂₈ O ₅ N ₂	70.7 (72.5)	5.5 (5.6)	5.2 (5.6)	10	8	10	8	8	8
III _c	<i>p</i> -Cl-Phenyl	147 (52)	C ₂₉ H ₂₅ O ₅ N ₂ Cl	66.5 (67.3)	4.8 (4.8)	5.1 (5.4)	14	16	16	14	16	14
III _d	<i>o</i> -Cl-Phenyl	128 (50)	C ₂₉ H ₂₅ O ₅ N ₂ Cl	67.1 (67.2)	4.5 (4.8)	5.2 (5.4)	16	16	18	16	16	16
III _e	Phenoxymethyl	105 (65)	C ₃₀ H ₂₈ O ₅ N ₂	72.0 (72.5)	5.5 (5.6)	5.2 (5.6)	14	12	12	12	12	12

* For names see text; *Stock solutions in propylene glycol (10 mg/10 ml); **Values include the diameter of the cup (6 mm) also; †Crystallization from acetone (II_b-II_p, II_j, II_l) benzene (II_d-III_d), C₆H₆-CHCl₃ (II_h, II_i), CH₃OH (II_k, III_b, III_c), AcOH (II_m).

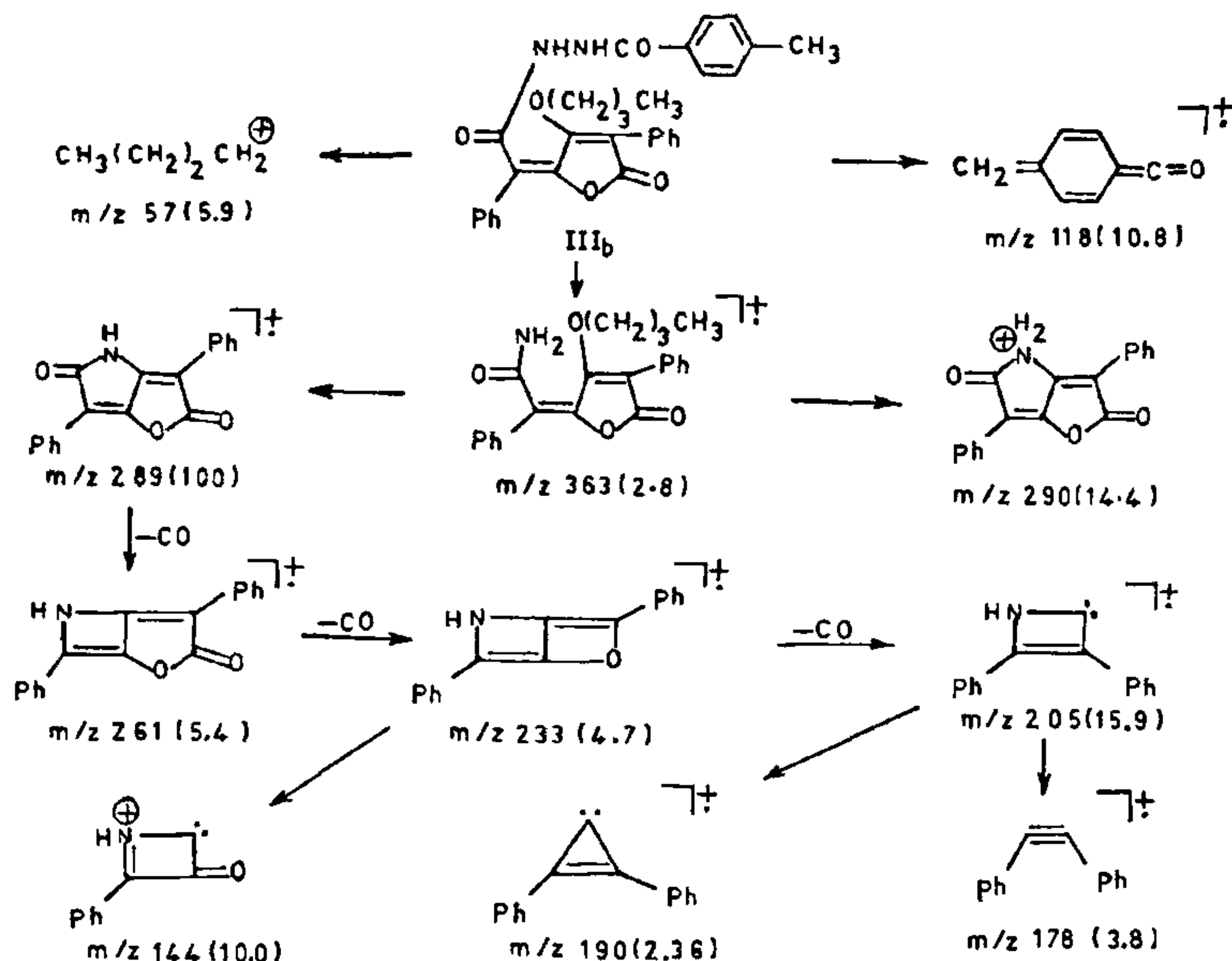


Chart 1.

General procedure for the preparation of II and III

A mixture of pulvinic dilactone (0.005 mol) and aromatic acid hydrazide (0.005 mol) was refluxed either in xylene (20 ml) or in *n*-butanol (15–20 ml) in the presence of catalytic amount of pyridine for 3 h. The solvent was removed under reduced pressure. The gummy nature of some products was removed by triturating with petroleum ether and if necessary by acidification with dil. HCl. The products were purified by recrystallization from appropriate solvents (table 1).

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RECORD OF INARTICULATE BRACHIOPODS FROM THE ARENACEOUS MEMBER OF THE TAL FORMATION, GARHWAL SYNCLINE, LESSER HIMALAYA, INDIA

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THIS note records the Lower Cambrian (Botomian Stage=? Tsanglangpuian) inarticulate brachiopods belonging to four genera, viz. *Magnicanalis*, *Obolella*, *Paterina* and *Obolopsis*, from the greyish siltstone unit of the Arenaceous Member of the Tal Formation exposed in a section south-east of Kauriyala village (30°03'N and 78°00'E) on the Rishikesh–Badrinath highway in the northern limb of the Garhwal Syncline (figure 1). Of late, this fossil horizon has also yielded redlichiid trilobites (under communication) and small shelly fossils¹. A similar Early Cambrian brachiopod assemblage was earlier reported from the basal part of the Phulchatti Member of the Tal Formation from Mussoorie Syncline, Uttar Pradesh^{2,3}, and Nigalidhar Syncline,