

Scheme 1

by benzoyloxy radical; hence the proportion of the product formed is increased. The reaction being carried out at lower temperature, the rate of the decomposition of the benzoyloxy radical is comparatively slower. It undergoes competing reactions such as the radical recombination and chain reaction, forming little benzoic acid, carbon dioxide, biaryl, etc.^{9,10}

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Palynological dating of a coal seam in Ayyanapalem area, Khammam District, Andhra Pradesh, India

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A palynological study of five subsurface samples of a coal seam near Ayyanapalem, Chintalapudi sub-basin of Godavari valley, Andhra Pradesh, was carried out. Twenty-five genera, including monosaccate, striate and nonstriate bisaccate, and trilete sporomorphs were identified; striate bisaccates predominate. Based on occurrence of *Rhizomaspora*, *Microbaculispora*, *Indotriradites*, *Crucisaccites* and *Corisaccites*, the coal seam is inferred to be similar in age to the Barakar Formation of the Lower Gondwana.

DURING a test drilling (GAG-1) (17°22'50"N, 80°40'E) for coal by the Geological Survey of India near Ayyanapalem, Chintalapudi sub-basin of Godavari valley, Khammam District, Andhra Pradesh, a 30-m thick coal seam (coal + carbonaceous shale) has been encountered at a depth of 27 m (Figure 1). This is a significant find as it opens up a favourable horizon for the exploration of coal in this area. Recent field work has established a succession of Talchir, Barakar and Kamthi formations of Lower Gondwana in this area¹.

A palynological study of five samples covering the entire coal seam has been undertaken with the purpose of assessing and evaluating the stratigraphic position of the coal-bearing formation. Twenty-five genera comprising monosaccate, striate and nonstriate bisaccate, monolete and trilete groups could be identified (Figure 2). The more significant

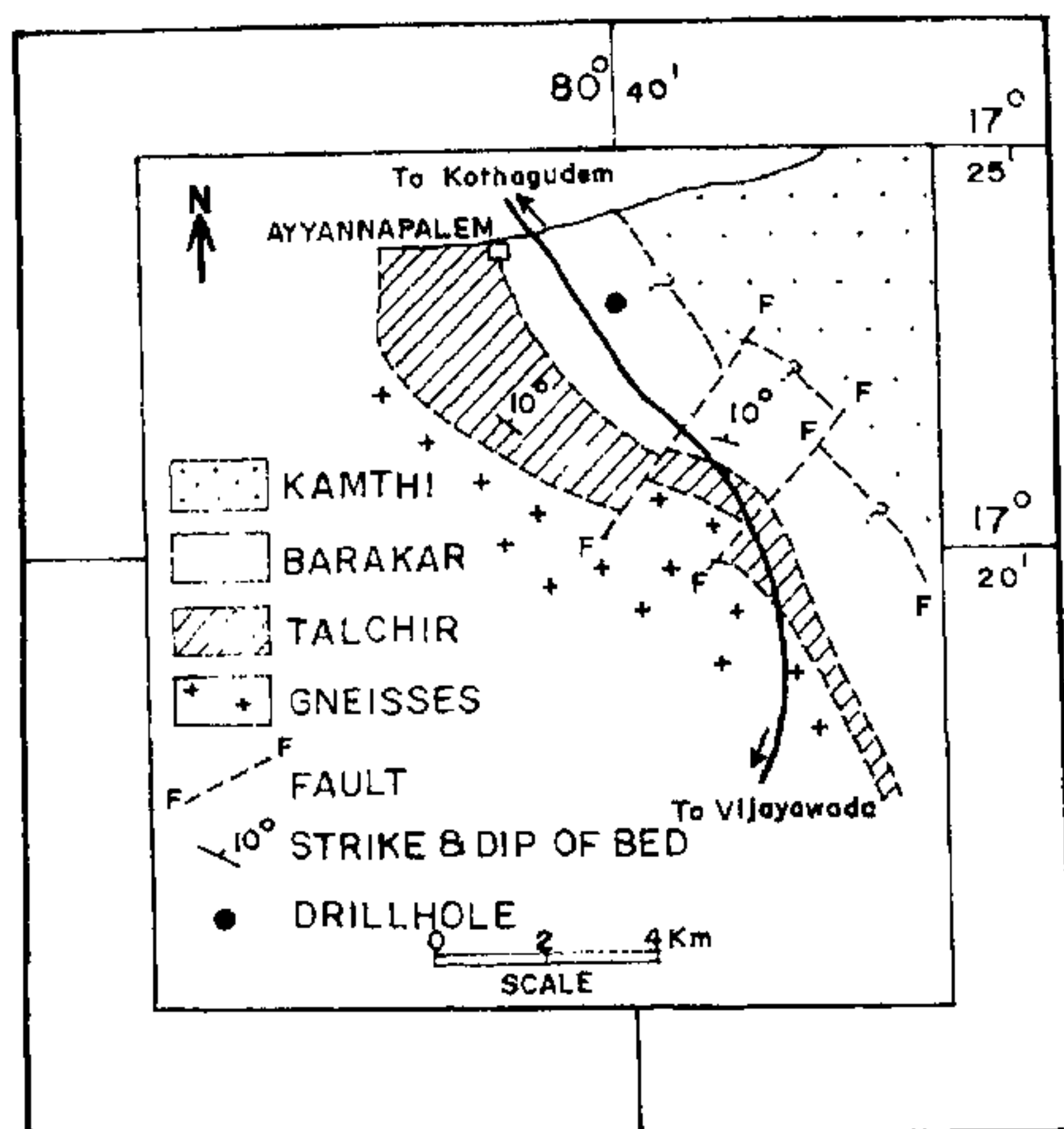


Figure 1. Geological map of Ayyanapalem area, Khammam District, Andhra Pradesh.

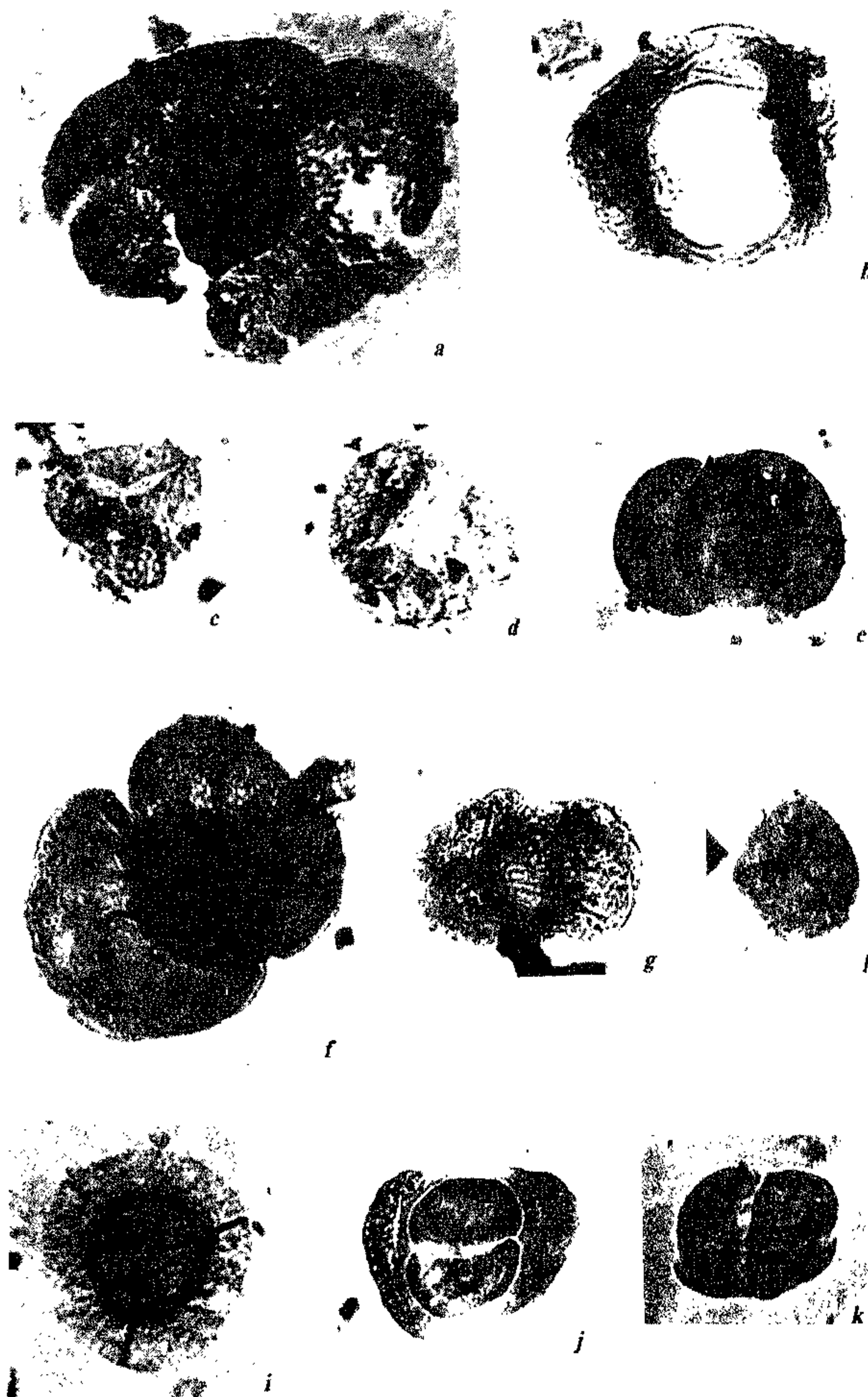


Figure 2. *a*, *Playsaccus* sp., Kar, 1968 ($\times 450$). *b*, *Striamonosaccites* sp., Bharadwaj, 1962 ($\times 450$). *c*, *Lophotrilete* sp., Tiwari, 1967 ($\times 500$). *d*, *Scheuringipollenites* sp., Tiwari, 1973 ($\times 450$). *e*, *Lueckisporites* sp., Tiwari, 1964 ($\times 450$). *f*, *Rhizomaspora* sp., Tiwari, 1964 ($\times 450$). *g*, *Striatites* sp., Tiwari, 1964 ($\times 450$). *h*, *Microbaculispora* sp., Tiwari, 1964 ($\times 500$). *i*, *Indotriradites* sp., Tiwari, 1964 ($\times 450$). *j*, *Lueckisporites* sp., Sinha, 1970 ($\times 450$). *k*, *Corisaccites* sp., Venkatachala & Kar, 1966 ($\times 450$).

palynotaxa of this assemblage are *Microbaculispora*, *Indotriradites*, *Cyclobaculispora*, *Acanthotriletes*, *Faunipollenites*, *Lahirites*, *Striatites*, *Rhizomaspora*, *Striatopodocarbites*, *Distriatites*, *Scheuringipollenites*, *Cuneatisporites*, *Densipollenites*, *Corisaccites* and *Vittatina*.

The striate bisaccates are the predominant elements of the assemblage but monosaccates are very few. Among

the triletes, *Indotriradites* is relatively more frequently found. Thus, the overall assemblage, with the striate bisaccates predominating, when taken in conjunction with the occurrence of *Rhizomaspora*, *Microbaculispora*, *Indotriradites*, *Crucisaccites* and *Corisaccites* clearly points toward the age relationship with Barakar Formation^{2,3}.

It may be noted that this is the first confirmed

palynological report of the Barakar Formation with coal occurrences in this area. Thus, recognition of Barakar Formation based upon field study is now corroborated by palynological study. Detailed investigation of the spore and pollen complex of the coal seam is under way.

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Anticancer drugs part III: New spin labelled derivatives of podophyllotoxin

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Three new spin labelled derivatives of podophyllotoxin, *N'*-deoxypodophyllic acid-*N*-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] thiosemicarbazide (GP-5,4), *N'*-picropodophyllic acid-*N*-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] thiosemicarbazide (GP-6,7) and deoxypodophyllic acid-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] hydrazone (GP-8,8) have been synthesized by the reaction of appropriate nitroxyls with hydrazides of podophyllotoxin.

PODOPHYLLOTOXIN (1) and a number of its derivatives possess anticancer activity and some of them have been extensively used clinically^{1,2}. Recently we have found³⁻⁶ that the introducing a stable nitroxyl moiety into the molecule of podophyllotoxin could result in compounds with pharmacological properties superior to those of the parent compounds. It was considered worthwhile to synthesize more spin labelled derivatives of podophyllotoxin to find out a new anticancer drug with high activity and low toxicity. Therefore, in the present work we have synthesized *N'*-deoxypodophyllic acid-*N*-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] thiosemicarbazide (GP-5,4), *N'*-picropodophyllic acid-*N*-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] thiosemicarbazide (GP-6,7) and deoxypodophyllic acid-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] hydrazone (GP-8,8).

N'-deoxypodophyllic acid-*N*-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] thiosemicarbazide (4), *N'*-picropodophyllic acid-*N*-[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] thiosemicarbazide (7) and deoxypodophyllic acid-[4-

(2,2,6,6-tetramethyl-1-piperidinyloxy)] hydrazone (8) were prepared as shown in Scheme 1.

Podophyllotoxin (1), isolated from a Chinese medicinal herb *Podophyllum emodi* Wall var. *Chinesis sprague*, was used as the starting material.

Podophyllotoxin (1) was converted to deoxypodophyllotoxin (2) by Pd/C catalytic reduction. Hydrazinolysis of 2 yielded deoxypodophyllic acid hydrazide (3). GP-5(4) was prepared by the reaction of 3 with isothiocyanide (9). The treatment of 3 with excess 2,2,6,6-tetramethyl-1-piperidinyloxy (10) gave GP-8(8). The picropodophyllic acid hydrazide (6) (ref. 7) obtained from the hydrazinolysis of picropodophyllotoxin (5) was converted to GP-6(7) under similar conditions.

All products were purified by chromatography on silica gel and checked by thin layer chromatography with 3-5 different solvent systems. Structural characterization is based on elemental analysis, MS, IR, UV and ESR data.

IR spectra were recorded on 5DX infrared spectrophotometer (ν_{\max}^{KBr} , cm^{-1}) and UV spectra on Beckman DU-7 ultraviolet visible spectrophotometer ($\lambda_{\max}^{\text{MeOH}}$, nm). MS data were obtained with a ZAB-HS mass spectrometer (important fragments are given with the relative intensities in the bracket), EPR data with Bruker ER-200D-SRC electron paramagnetic resonance spectrometer (X band, modulation frequency of 12.5 kHz, microwave power of 5 mW) and elemental analysis data

