

tively tedious and time-consuming. An alternative method, based on chemical reduction of corrosion products by the use of alkaline dithionate solution in the absence of atmospheric oxygen⁴, motivated us to search for a new type of reducing agent which can be used for conservation.

Indo-Sassanian coins (550–700 A.D.)⁵ were found in great numbers in Rajasthan, Gujarat, and Malwa and parts of Uttar Pradesh and Bihar. Eleven hundred coins were obtained from Mr K. K. Maheshwari, Indian Institute of Research in Numismatic Studies, Anjaneri, Nasik, for cleaning and conservation. The surfaces of all these coins were covered by green- and grey-coloured corrosion products. Some of the coins were fused together due to corrosion (figure 1).

The coins were first thoroughly washed with distilled water till the superficial dirt and dust were removed. After washing, the coins were immersed in 2 l of a 1% aqueous solution of hydrazine hydrate in a plastic container. The oxide layer reacts with the hydrazine and undergoes reduction. The coins were then washed thoroughly with distilled water and the red powdery coating rubbed off with a soft brush. The coins were then immersed in 1% alcoholic benzotriazole solution for about an hour and dried in air. Benzotriazole forms a complex coating on the surface which protects the coins from further corrosion. Finally all the coins were given a poly-vinyl acetate coating.

The chemical analysis of these Indo-Sassanian coins shows that they are made mainly of Cu-Ag alloy. Figures 1 and 2 show the state and condition of the coins before and after treatment. Eleven hundred silver-coated copper coins treated by this method gave 96 mg of silver from the decanted solutions, which is not a significant loss of silver coating.

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CHEMICAL EXAMINATION OF THE BROWN ALGA *STOECHOSPERMUM MARGINATUM* (C. AGARDH)

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CHEMICAL investigation of the brown alga *Stoechospermum marginatum* (family Dictyotaceae) led to the isolation and characterization of three steroidal constituents and a fatty ester along with five fatty acids on the basis of chemical and spectroscopic evidence.

During the general screening for pharmacological activity of marine algae from the west coast of India, the crude methanolic extract of *S. marginatum* was found to have spasmolytic activity¹; it has also been reported to inhibit the growth of *Staphylococcus aureus*². Our search for the pharmacologically active principle led to the isolation of steroids, fatty acids and an ester characterized on the basis of GC, IR, ¹H NMR and mass spectra. The results of the analyses are being reported in this communication.

The dried alga (4 kg) was extracted thrice with methylene chloride to yield 70 g of dark-green, viscous oil. Column chromatography over alumina afforded compounds A, B and C.

Glacial acetic acid eluate yielded a mixture of fatty acids (2.8 g). The esterified acid mixture (diazomethane) on comparative GC analysis with authentic samples (relative retention times) indicated the presence of myristic (30.6%), palmitic (60%), stearic (1.6%), oleic (0.097%) and heptadecanoic (0.132%) acids as their esters.

Compound A — Ethyl palmitate:

The IR spectrum revealed the presence of > C=O group (1730 cm⁻¹), 1165, 1110, 1030 and 720 cm⁻¹; mass *M*⁺ at *m/e* 284 (C₁₈H₃₆O₂), *m/e* 88 (base peak characteristic of ethyl ester) and the separation of units of the fragments by 14 mass units. The ¹H NMR spectrum showed signals at δ 0.75, 1.2, 3.5 and a multiplet centred at 4. All these data indicated that the compound was ethyl palmitate.

Compound B:

White solid m.p. 124°, acetate m.p. 118° gave positive Liebermann-Burchard test; analysed for C₂₉H₄₈O, *M*⁺*m/e* 412 and its IR and ¹H NMR spectra showed the following bands IR—3450 and 1035 cm⁻¹ (—OH), 1350 and 1370 cm⁻¹ (isopropyl),

790 and 830 cm^{-1} (Δ^5 bond in sterols) and 810 cm^{-1} (H atom on trisubstituted double bond); NMR bands at δ 5.3 (*m*, $\text{C}_6\text{-H}$); 0.66 (*s*, 3H, C_{18}), 0.9 (*s*, 3H, C_{19}); 1.59 (*d*, 6 Hz, 3H, C_{20}); 5.1 (1H, $J = 6\text{ Hz}$, 9), 2.2 (1H, allylic, C_{25}); 0.95 (*d*, 6H, $\text{>C}=\text{C}(\text{CH}_3)$), 3.4 ($\text{C}_{3\alpha}$, 1H, *m*), mass *m/e* 412, (M^+), 314 (base peak) and triplet at *m/e* 299, 300 and 301 (indicative of $\Delta^{24,28}$ double bond). These are well in agreement with the data reported for fucosterol³, and hence it was characterized as fucosterol.

The mass spectrum of fucosterol also showed the presence of dihydrofucosterol (m^+ 414). Fucosterol, a major sterol of *S. marginatum*, has been reported to be non-toxic and has the ability to reduce blood cholesterol level⁴. It has also been known to induce sexual reproduction in the *Ascomycetes* fungus, *Phytophthora cactorum*⁵. This steroid may become significantly important as a base material for the manufacture of sex hormones and for steroid synthesis⁶.

Compound C — 24-ketocholesterol:

IR bands at 1710 cm^{-1} (>C=O), *m/e* at 400, (m^+), 43 (base peak), 382, 314, 271, 255, 213, 159, 145, 133, 119 and 107. Mass spectral data agreed with the data reported for 24-ketocholesterol⁷. It is possible that this steroid may be an artifact as reported by Knights⁸, since the sample was air-dried prior to extraction and is present in trace quantities.

This is the first report of the isolation of three steroidal constituents from *S. marginatum*.

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ICHOGENUS SKOLITHOS FROM GETHIA UNIT, DISTRICT NAINITAL, KUMAUN LESSER HIMALAYA

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THE Nainital syncline comprises Nagthat–Blaini–Krol–Tal sedimentaries in an ascending order of succession. The rocks were studied as early as 1890 by Middlemiss. Subsequently, the geology of the area has been studied by many workers. However, the lithostratigraphic setting of the Nainital area is still controversial. The rocks around Gethia are extensively deformed as a result of multiplicity of faults and thrusts owing to its proximity with Main Boundary Thrust (figure 2), and stratigraphic position of the rocks is very ambiguous. It was Dhaundiyal who for the first time recognized a succession of a fossiliferous limestone and shales and grouped the rocks into what he named the Gethia horizon.

Exposed SE of Nainital around Gethia ($29^{\circ}21'42''$: $79^{\circ}29'47''$) trending NW–SE and dipping $25\text{--}35^{\circ}$ due NW (figures 1 and 2), the unit has been a matter

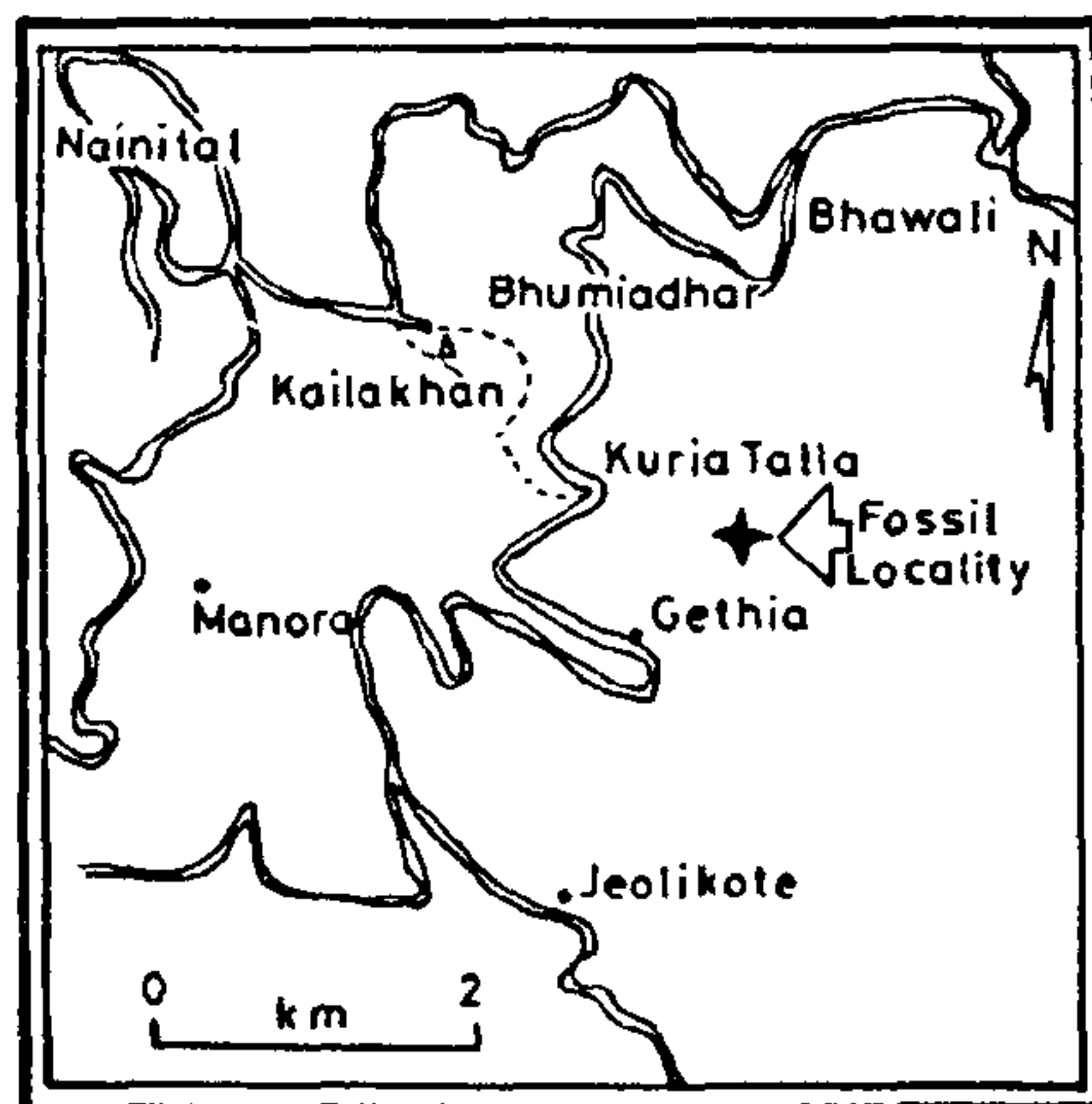


Figure 1. Location map of the fossil locality.