

aromatic,  $J = 3$  Hz), 6.55 (s, 1H, C<sub>8</sub>-H aromatic), 6.65 (s, 1H, C<sub>5</sub>-H aromatic).

MS:  $m/z$ -412 [ $M^+$  (70%)], 410 [ $(M^+ - 2H)$ (35%)], 378 [ $(M^+ - H_2S)$ (100%)], 350 [ $(M^+ - O = C = S \& 2H)$  (30%)]

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## A NOVEL METHOD FOR CLEANING AND CONSERVATION OF CORRODED SILVER-COATED COPPER COINS

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THE conservation of ancient copper alloys is often complicated by the presence of decorations and coatings of other metals like gold, silver and tin. These decorations are concealed in heavy incrustations of a corroded metal. As these coatings and decorations are of great archaeological significance, it is important to preserve them as well as possible. It is necessary to look for a new cleaning method to retain the decorations, inscriptions and die-stamps present on artifacts and coins.

A new method for conservation of ancient silver-coated copper coins has been developed. The method is based on the chemical reduction of corro-

sion (oxidation) products of copper and silver by using hydrazine hydrate,  $NH_2-NH_2.H_2O$ . This method is quick, simple and inexpensive, and renders the inscriptions and other details on the coins quite clear and even better than do the earlier methods. The treatment can be carried out even in the presence of atmospheric oxygen and can be applied to any number of artifacts and coins in one lot.

Silver decorations on bronze survive without corrosion because of cathodic protection, but their preservation during cleaning is difficult. Earlier methods<sup>1-3</sup> of treating silver-coated corroded bronzes are not suitable because of the dissolution of the corroded layers including the silver coating. The electrochemical reduction methods are rela-



Figures 1 and 2. 1. Before treatment, and 2. After treatment.

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 oxygen<sup>4</sup>, motivated us to search for a new type of reducing agent which can be used for conservation.

Indo-Sassanian coins (550–700 A.D.)<sup>5</sup> 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 activity<sup>1</sup>; it has also been reported to inhibit the growth of *Staphylococcus aureus*<sup>2</sup>. 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, <sup>1</sup>H 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<sup>-1</sup>), 1165, 1110, 1030 and 720 cm<sup>-1</sup>; mass *M*<sup>+</sup> at *m/e* 284 (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>), *m/e* 88 (base peak characteristic of ethyl ester) and the separation of units of the fragments by 14 mass units. The <sup>1</sup>H 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 C<sub>29</sub>H<sub>48</sub>O, *M*<sup>+</sup>*m/e* 412 and its IR and <sup>1</sup>H NMR spectra showed the following bands IR—3450 and 1035 cm<sup>-1</sup> (—OH), 1350 and 1370 cm<sup>-1</sup> (isopropyl),