Compound (1) formed a monomethyl ether (Me₂SO₄–K₂CO₃), (2), m.p. 130–133°C [found C, 66.45; H, 5.24; OMe (Zeisel’s method), 36.19; C₁₇H₁₈O₆ required C, 66.66; H, 5.26, 4 x OMe (Zeisel’s method), 36.25%] and monocatec (Ac₂O–C₃H₅N), (3), m.p. 140–142°C [found C, 64.78; H, 4.80; C₂₀H₁₈O₇ required C, 64.86; H, 4.86%], confirming the presence of one hydroxyl group in (1). It gave an orange colour with magnesium acetate soluble in 2% aq. Na₂CO₃, showing the presence⁴ of hydroxyl at position-3. Chromic acid oxidation of (1) gave 4,5-dimethoxyphenol acid, m.p. 173–174°C (Lit. m.p., 175°C, m.m.p. and Co-TLC), as one of the oxidation products, showing the presence of 2 x MeO at C-6 and C-7 positions. The major MS fragment ions of (1) were as follows: MS m/z(%): 328 (M⁺, 50), 313(80), 311(90), 310(65), 300(25), 299(22), 272(100), 216(85), 165(40) and 137(20), which confirms the structure of eugenone as (1).

1: R = H, 2: R = Me, 3: R = Ac

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1. The wealth of India, CSIR, New Delhi, 1966.

THIONATION OF β-APOPICROPODOPHYLLIN

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Podophyllotoxin (1)⁴, a naturally occurring lignan lactone with a phenyl tetralin system is a well-known antimitotic agent². The dehydration product, β-apopicropodophyllin (2)³, from podophyllotoxin is 500 times more antimitotic than podophyllotoxin itself. It was considered worthwhile to convert the lactone moiety of (2) to thiolactone and to study the antimitotic activity of the product.

Lawesson's reagent (3) is a good thionating agent⁴,⁵, selective over phosphorus pentasulphide in the quantitative transformation of lactone to thiolactone. We have successfully converted (2) to thio-β-apopicropodophyllin (4) by heating (2) with (3) in anhydrous xylene, with 65% yield. The formation of (4) is evident from the fact that the molecular ion peak of the product appears at m/z 412 and the IR spectrum shows a peak at 1220 cm⁻¹, due to conjugated C = S stretching⁶, while absorption due to the C = O group is absent.

The melting point reported is uncorrected. The IR spectrum was recorded on a Perkin Elmer model 157, the PMR spectrum on a Varian T-60 using TMS as internal standard, and the mass spectrum on a Hitachi RMU-61 spectrometer. The compound was checked for purity by TLC on silica gel plates.

**Experimental**

β-apopicropodophyllin (0.1 g, 0.0025 mol) and Lawesson's reagent (0.09 g, 0.0026 mol) in anhydrous xylene (2 ml) were heated at 125°C for 10 h. The reaction mixture was cooled and washed with water (4 × 5 ml) and xylene was evaporated by using a rotary evaporator. The gummy residue obtained was purified by passing it through a silica gel column using chloroform as eluant. After evaporation the compound was recrystallised with CCl₄.

Yield 0.068 g (65%), m.p. 111–114°C. IR (nujol): 1660 (–C = C–), 1600 (aromatic –C = C–), 1220 (conjugated –C = S) cm⁻¹.

PMR (CDCl₃): δ 3.75 (s, 1H, –OCH₃, C₁–H₁), 4.75–4.9 (s, 3H, lactone CH₂, C₁–H₁), 5.85 (v, 2H, –O–CH₂–O–), 6.35 (d, 2H, C₂H, and C₆H)
aromatic, \( J = 3 \text{ Hz} \), 6.55 (s, 1H, C\textsubscript{8}–H aromatic), 6.65 (s, 1H, C\textsubscript{3}–H aromatic).

MS; \( m/z = 412 \ [M^+ (70\%)] \), 410 [(M\textsuperscript{+}–2H)(35%)], 378 [(M\textsuperscript{+}–H\textsubscript{2}S)(100\%)], 350 [(M\textsuperscript{+}–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 corrosion (oxidation) products of copper and silver by using hydrazine hydrate, \( \text{NH}_2–\text{NH}_2\cdot\text{H}_2\text{O} \). 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\textsuperscript{1–3} 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](image_url)