

Table 1 Yield, m.p. and PMR data

Styryl dyes	Yield %	M p. °C (solvent)	PMR (CDCl ₃) δ
2a	54	102-103 (Benzene)	1.23(<i>t</i> , 3H, CH ₂ -CH ₃ , <i>J</i> = 6 Hz) 4.00(<i>q</i> , 2H, CH ₂ -CH ₃ , <i>J</i> = 6 Hz) 7.06-7.86(<i>m</i> , 5H, aromatic protons) and 10.85(<i>s</i> , 1H, C ₆ H ₅ -CH=)
2b	59	115-116 (Chloroform)	1.25(<i>t</i> , 3H, CH ₂ -CH ₃ , <i>J</i> = 6 Hz), 4.17(<i>q</i> , 2H, CH ₂ -CH ₃ , <i>J</i> = 7.5 Hz), 6.70(<i>d</i> , 1H, C ₆ H ₅ -CH=CH-, <i>J</i> = 12 Hz) 6.84(<i>d</i> , 1H, C ₆ H ₅ -CH=, <i>J</i> = 15 Hz) 7.40-7.57(<i>m</i> , 5H, aromatic protons) and 7.92(<i>d</i> , 1H, -CH=CH-CH=, <i>J</i> = 12 Hz)
2c	62	126-127 (Chloroform)	1.25(<i>t</i> , 3H, CH ₂ -CH ₃ , <i>J</i> = 7.5 Hz) 2.95(<i>s</i> , 6H, -N(CH ₃) ₂), 4.00(<i>q</i> , 2H, CH ₂ -CH ₃ , <i>J</i> = 6 Hz), 6.20-6.55(<i>m</i> , 3H, C ₆ H ₄ -CH=CH-), 7.00-7.30(<i>m</i> , 3H, C ₆ H ₄ -CH=CH-), and 9.20(<i>d</i> , 1H, -CH=CH-CH=, <i>J</i> = 9 Hz).

All the m.ps are uncorrected. Satisfactory elemental analysis were obtained for all compounds. NMR spectra were recorded on a spectrometer (Varian-90 MHz) with TMS as internal standard.

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EUGNONE, A NEW ANTHRAQUINONE FROM THE STEM BARK OF *SAPIUM EUGNIFOLIUM*

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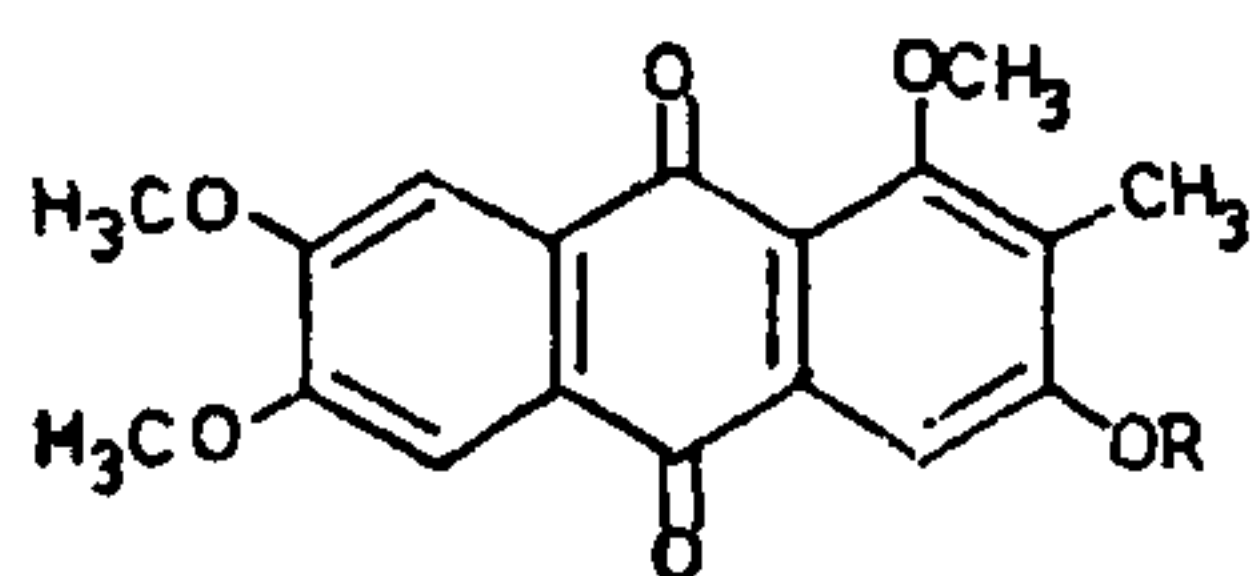
SAPIUM EUGNIFOLIUM Linn. (Euphorbiaceae) is used in the Indian system of medicine¹. Anthraquinone has not been reported so far from this plant. We report here the isolation of a new anthraquinone eugnone (3-hydroxy-1, 6, 7-trimethoxy-2-methyl anthraquinone) and its characterization by colour

reactions, spectral data and chemical methods.

The powdered stem bark of *S. eugnifolium* (3 kg) was extracted with ethanol under reflux from 180 h on a water bath. The ethanol from the percolates (20l) was removed under reduced pressure on a water bath to get a syrupy mass which was then successively extracted with petroleum ether, benzene, chloroform and ethyl acetate. The excess of solvent was removed from the ethyl acetate extract under reduced pressure to get a yellowish solid mass which on TLC examination showed the presence of a single entity. It was loaded on a column of neutral alumina, eluted with CHCl₃-EtOAc (8:2) and crystallized as yellow coloured crystals from CHCl₃-MeOH (8:2):eugnone, (1), (yield 900 mg).

Eugnone (1), m.p. 278-280°C, C₁₈H₁₆O₆ (*M*⁺328), showed UV-visible absorption maxima at 225, 250, 380, 405 nm and gave a positive Borntrager reaction² characteristic for an anthraquinone. The IR (KBr) spectrum of (1) showed characteristic absorptions for hydroxyl (3250-3350 cm⁻¹), methoxyl (2900), methyl (2830 and 1470) and carbonyl (1690) groups. The ¹H NMR spectrum (DMSO-*d*₆, δ, 90 MHz) of (1) showed a signal for an unchelated hydroxyl (11.20), three methoxyls (4.0) and one methyl group (2.40)³. Further, (1) showed two separate singlets (δ 8.16, 7.50 and 7.66) corresponding to one proton, at positions C-5 and C-8, and C-4, respectively.

Compound (1) formed a monomethyl ether ($\text{Me}_2\text{SO}_4\text{-K}_2\text{CO}_3$), (2), m.p. 130–133°C [found C, 66.45; H, 5.24; OMe (Zeisel's method), 36.19; $\text{C}_{19}\text{H}_{18}\text{O}_6$ required C, 66.66; H, 5.26, 4 x OMe (Zeisel's method), 36.25%] and monoacetate ($\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$), (3), m.p. 140–142°C [found C, 64.78; H, 4.80; $\text{C}_{20}\text{H}_{18}\text{O}_7$ 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. Na_2CO_3 , showing the presence⁴ of hydroxyl at position-3. Chromic acid oxidation of (1) gave 4,5-dimethoxyphthalic 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 eugone as (1).



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

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THIONATION OF β -APOPICROPODOPHYLLIN

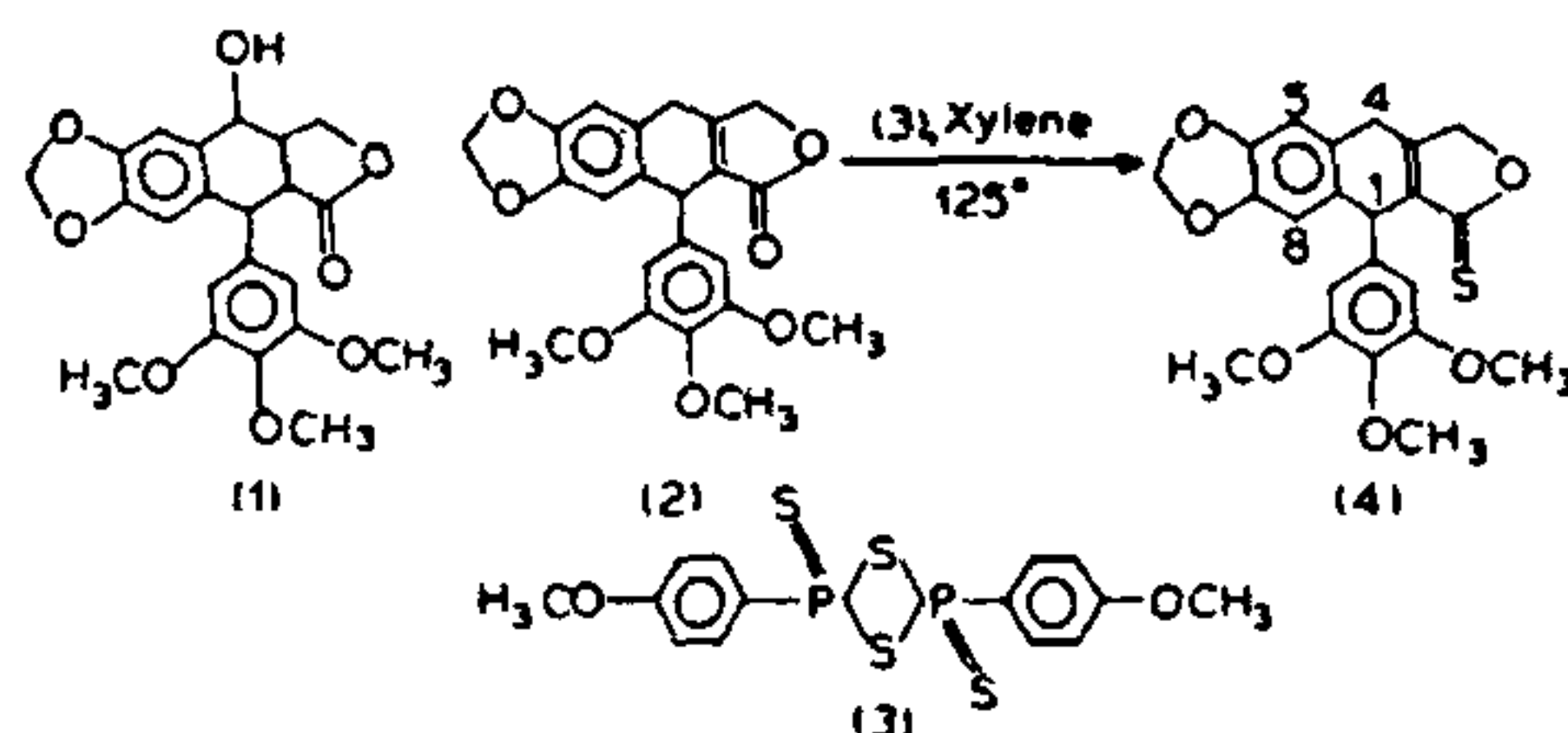
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PODOPHYLLOTOXIN (1)¹, a naturally occurring lignan lactone with a phenyl tetralin system is a well-

known antimitotic agent². The dehydration product, β -apopicropodophyllin (2)³, from podophyllo-toxin is 500 times more antimitotic than podophyllo-toxin 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 agent^{4,5}, 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 1220cm^{-1} , due to conjugated $-\text{C}=\text{S}$ stretching⁶, while absorption due to the $\text{C}=\text{O}$ 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 x 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 CCl_4 .

Yield 0.068 g (65%), m.p. 111–114°. IR (nujol): 1660 ($-\text{C}=\text{C}-$), 1600 (aromatic $-\text{C}=\text{C}-$), 1220 (conjugated $-\text{C}=\text{S}$) cm^{-1} .

PMR (CDCl_3); δ 3.75 (s, 11H, $-\text{OCH}_3$, $\text{C}_4\text{-H}$), 4.75–4.9 (s, 3H, lactone CH_2 , $\text{C}_1\text{-H}$), 5.85 (s, 2H, $-\text{O}-\text{CH}_2-\text{O}-$), 6.35 (d, 2H, C_2H , and C_6H