

## SYNTHESIS OF LINEAR PYRANOCOUMARINS: 4-METHOXY- AND 4,5-DIMETHOXY-XANTHYLETIN

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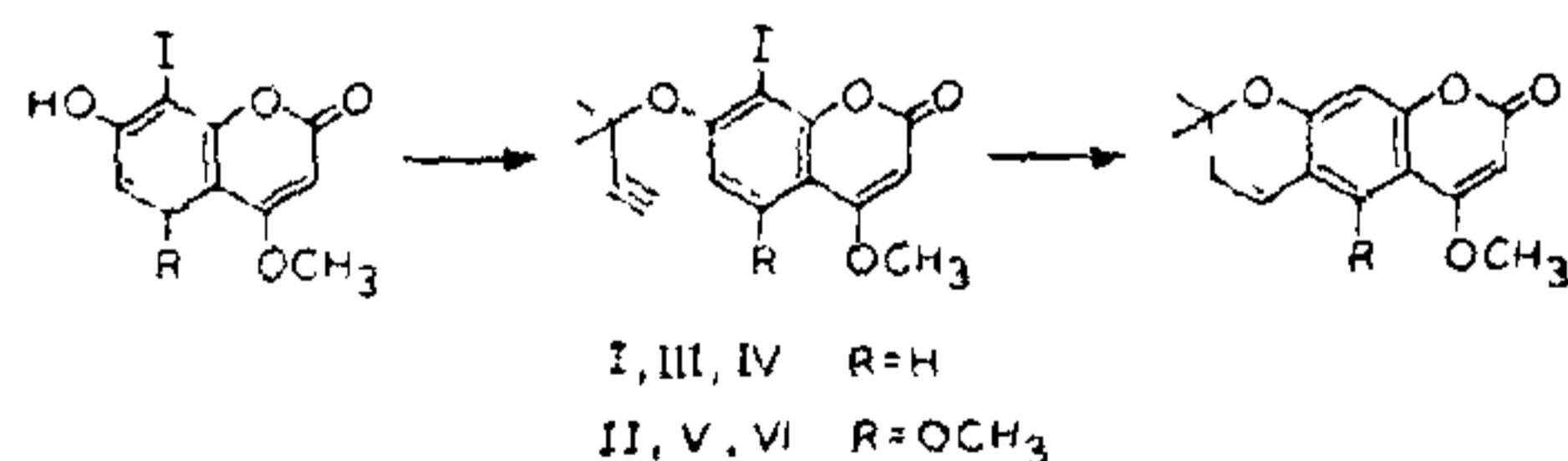
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THE natural occurrence of linear pyranocoumarins (xanthyletins), known for their marked physiological activities<sup>1,2</sup> is well reported<sup>3</sup>. The known synthesis of these compounds<sup>4-7</sup> involves many steps and the yield is poor. This difficulty is mitigated<sup>8</sup> by blocking an easily introducible and removable substituent, iodine. This method has now been applied for the synthesis of 4-methoxyxanthyletin (I) and 4,5-dimethoxyxanthyletin (II).

Propynylation of 7-hydroxy-8-iodo-4-methoxy-2H-1-benzopyran-2-one<sup>9</sup> (III) (prepared by iodination of 7-hydroxy-4-methoxy-2H-1-benzopyran-2-one with iodine and periodic acid in ethanol) with 3-chloro-3-methylbut-1-yne in acetone-K<sub>2</sub>CO<sub>3</sub> gave 8-iodo-4-methoxy-7-(1,1-dimethyl-2-propynyloxy)-2H-1-benzopyran-2-one (IV). Compound IV when boiled with N,N-dimethylaniline, afforded I. The structure of I was established by its <sup>1</sup>H NMR spectrum which showed two one proton singlets for H-5 and H-10. Other usual signals indicated that cyclization took place at 6-position with the elimination of iodine from 8-position.

Similarly, propynylation of 7-hydroxy-8-iodo-4,5-dimethoxy-2H-1-benzopyran-2-one<sup>10</sup> (V) with 3-chloro-3-methylbut-1-yne in acetone-K<sub>2</sub>CO<sub>3</sub> yielded 8-iodo-4,5-dimethoxy-7-(1,1-dimethyl-2-propynyloxy)-2H-1-benzopyran-2-one (VI) which on cyclization with N,N-dimethylaniline furnished the required II. The structure of II was in agreement with its <sup>1</sup>H NMR spectral data.



8-iodo-4-methoxy-7-(1,1-dimethyl-2-propynyloxy)-2H-1-benzopyran-2-one (IV) and 8-iodo-4,5-dimethoxy-7-(1,1-dimethyl-2-propynyloxy)-2H-1-benzopyran-2-one (VI).

A solution of 7-hydroxy-8-iodo-4-methoxy-2H-1-benzopyran-2-one<sup>9</sup> (III) or 7-hydroxy-8-iodo-4,5-dimethoxy-2H-1-benzopyran-2-one (V) (1 g; 0.0032 mol) in dry acetone (75 ml) was refluxed for 24 hr with 3-chloro-3-methylbut-1-yne (0.62 g; 0.006 mol) in the presence of K<sub>2</sub>CO<sub>3</sub> (anhyd.) (3 g) and KI (1.5 g). The solvent was distilled off and the residue treated with ice. The separated solid was filtered, washed and crystallized from benzene/petroleum ether to give IV or VI as colourless needles. Their characterization data are as follows:

IV: Yield 80%; m.p. 167–69°C  
<sup>1</sup>H NMR: δ 1.68 [s, 6H, C(CH<sub>3</sub>)<sub>2</sub>], 2.63 (s, 1H, C≡CH), 3.8 (s, 3H, OCH<sub>3</sub>), 7.02 (d, J = 9.5 Hz, 1H, H-6), 7.60 (d, J = 9.5 Hz, 1H, H-5).

VI: Yield 75%; m.p. 172–73°C  
<sup>1</sup>H NMR: δ 1.75 [s, 6H, C(CH<sub>3</sub>)<sub>2</sub>], 2.69 (s, 1H, C≡CH), 3.86 (s, 3H, 5OCH<sub>3</sub>), 3.9 (s, 3H, OCH<sub>3</sub>), 5.5 (s, 1H, H-3), 7.26 (s, 1H, H-6).

8,8-Dimethyl-4-methoxy-2H,8H-benzo[1,2-b:5,4-b']dipyran-2-one (I) and 4,5-dimethoxy-8,8-dimethyl-2H,8H-benzo[1,2-b:5,4-b']dipyran-2-one (II).

The above propynyl ether IV or VI (0.2100 g; 0.00056 mol) was refluxed with N,N-dimethylaniline (10 ml) for 3 hr. The cooled reaction mixture was poured over ice cold 5% hydrochloric acid. The solid separated was filtered, washed successively with 5% HCl and water, dried and crystallized from benzene-petroleum-ether to give I or II as white shining needles. Their characterization data are as follows:

I: yield, 50%; m.p. 138–40°C  
<sup>1</sup>H NMR: δ 1.42 and 1.50 (each s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 3.95 (s, 3H, OCH<sub>3</sub>-4), 5.47–5.6 (m, 2H, H-3 and H-7), 6.27 (d, J = 10 Hz, 1H, H-6), 6.30 (s, 1H, H-10), 7.35 (s, 1H, H-5).

II: yield, 45%; m.p. 195–98°C  
<sup>1</sup>H NMR: δ 1.43 and 1.50 (each s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 3.75 (s, 3H, OCH<sub>3</sub>), 3.9 (s, 3H, OCH<sub>3</sub>), 5.42–5.62 (m, 2H, H-3 and H-7), 6.2 (s, 1H, H-10), 6.5 (d, J = 10 Hz, 1H, H-6).

All melting points are uncorrected. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Perkin-Elmer R-32 (90 MHz) spectrometer using SiMe<sub>4</sub> as an internal standard. The C and H analysis for the compounds I–VI were within ±1% of the theoretical values.

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- Chakraborty, A., Des Gupta, A. and Bose, P. K., *Ann. Biochem. Exp. Med.*, 1957, **17**, 59.
- Joshi, B. S., Viswanathan, N., Kaul, C. L. and Grewal, P. S., *Indian J. Chem.*, 1980, **B19**, 495.

3. Dean, F. M., *Naturally occurring oxygen ring compound*, Butterworths, London, 1963, p. 198.
4. Jain, A. C. and Jain, S. M., *Tetrahedron*, 1973, **29**, 2803.
5. Mowat, D. and Murray, R. D. H., *Tetrahedron*, 1973, **29**, 2943.
6. Mulubuck, J., Ritchie, E. and Taylor, W. C., *Tetrahedron Lett.*, 1969, 1369.
7. Spath, E. and Hillel, R., *Ber. Dtsch. Chem. Ges.*, 1939, **72**, 2093.
8. Ahluwalia, V. K., Bhat, K. and Prakash, C., *Mh. Chem.* 1981, **112**, 119.
9. Ahluwalia, V. K., Prakash, C. and Singh, R. P., *Aust. J. Chem.*, 1979, **32**, 1361.
10. Ahluwalia, V. K., Prakash, C. and Singh, R. P., *Tetrahedron*, 1979, **35**, 2081.

### UNUSUAL CURRENT-POTENTIAL RELATIONSHIP AND MORPHOLOGY OF ELECTRODEPOSITS ON METALLIC GLASSES

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AN unusual electrokinetic and morphological observation was made on Cu-Zr metallic glasses. 2-Mercaptoethanol (MTEG) and 2-thiouracil (TUL) were used as additives in the acid copper sulphate bath. Remarkable changes in the electrokinetic parameters followed by growth habit modification were observed in the case of MTEG and TUL. Such studies are important in understanding the basic growth mechanism of the metallic glass-solution interface.

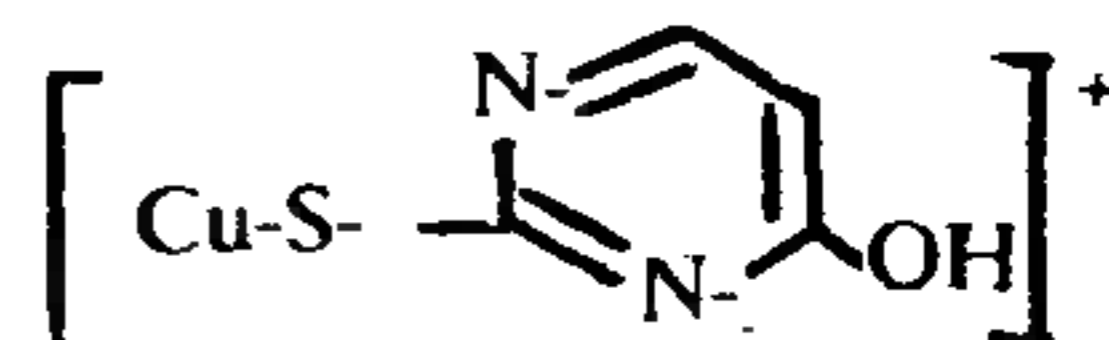
The surface of Cu-Zr metallic glass of compositions  $\text{Cu}_{60}\text{-Zr}_{40}$  and  $\text{Cu}_{75}\text{-Zr}_{25}$  was electropolished<sup>1</sup>. Electrodepositions were carried out at 2, 5, 10, 15, 20 and 30  $\text{mA cm}^{-2}$  to a thickness of 3.6  $\mu$  from a highly purified<sup>2</sup> bath (0.25 M  $\text{CuSO}_4$  + 0.1 M  $\text{H}_2\text{SO}_4$ ) with a known concentration of the addition agent when ever desired. The overpotentials ( $\eta$ ) were measured with respect to a freshly prepared copper reference electrode. The other experimental details have been described elsewhere<sup>3</sup>. Scanning electron micrographs of the electrodeposits were taken and examined.

The  $\eta$ - $\log i$  relationship was linear in pure solution with a slope of 116.4 mV with  $\text{Cu}_{60}\text{-Zr}_{40}$  and 136.4 mV with  $\text{Cu}_{75}\text{-Zr}_{25}$  metallic glass and the exchange current density values being 2.0 and

1.7  $\text{mA cm}^{-2}$ . Interestingly, the presence of MTEG and TUL in the electrolytic bath lowers the Tafel slope and the exchange current density.

In the case of MTEG, from  $10^{-10}$   $\text{mol dm}^{-3}$  to  $10^{-4}$   $\text{mol dm}^{-3}$ , the Tafel slopes observed were 99.18, 98.0, 94.48, 86.08, 70.0, 58.1 and 50.0 mV. The exchange current density at the above concentrations was 1.3, 1.6, 0.8, 0.7, 0.5, 0.4 and 0.4  $\text{mA cm}^{-2}$ . With TUL, from  $10^{-6}$   $\text{mol dm}^{-3}$  to  $10^{-3}$   $\text{mol dm}^{-3}$ , the observed values of the Tafel slope were 132.9, 101.4, 96.3 and 43.8 mV. The exchange current density at these concentrations was 2.2, 4.6, 1.5 and 1.4  $\text{mA cm}^{-2}$ .

This unusual current-potential relationship is attributed to the formation of  $[\text{Cu-S-CH}_2\text{-CH}_2\text{-OH}]^+$  electron donor-acceptor complex. This is confirmed by the IR spectral data of the scraped electrodeposit which reveals the disappearance of the absorption peak at  $2550 \text{ cm}^{-1}$  involving the -SH group in the presence of MTEG. Similarly, in the case of TUL, the changes in the electrokinetic parameters are due to the formation of



electron donor-acceptor complex confirmed by the IR spectra.

Further, the complex formed in the case of MTEG and TUL may degrade to give  $\text{Cu}^+$  ions facilitating a rapid metal ion transfer leading to a single electron transfer, instead of a two-electron transfer, in steps, as suggested by Conway and Bockris<sup>4</sup> in pure solution.

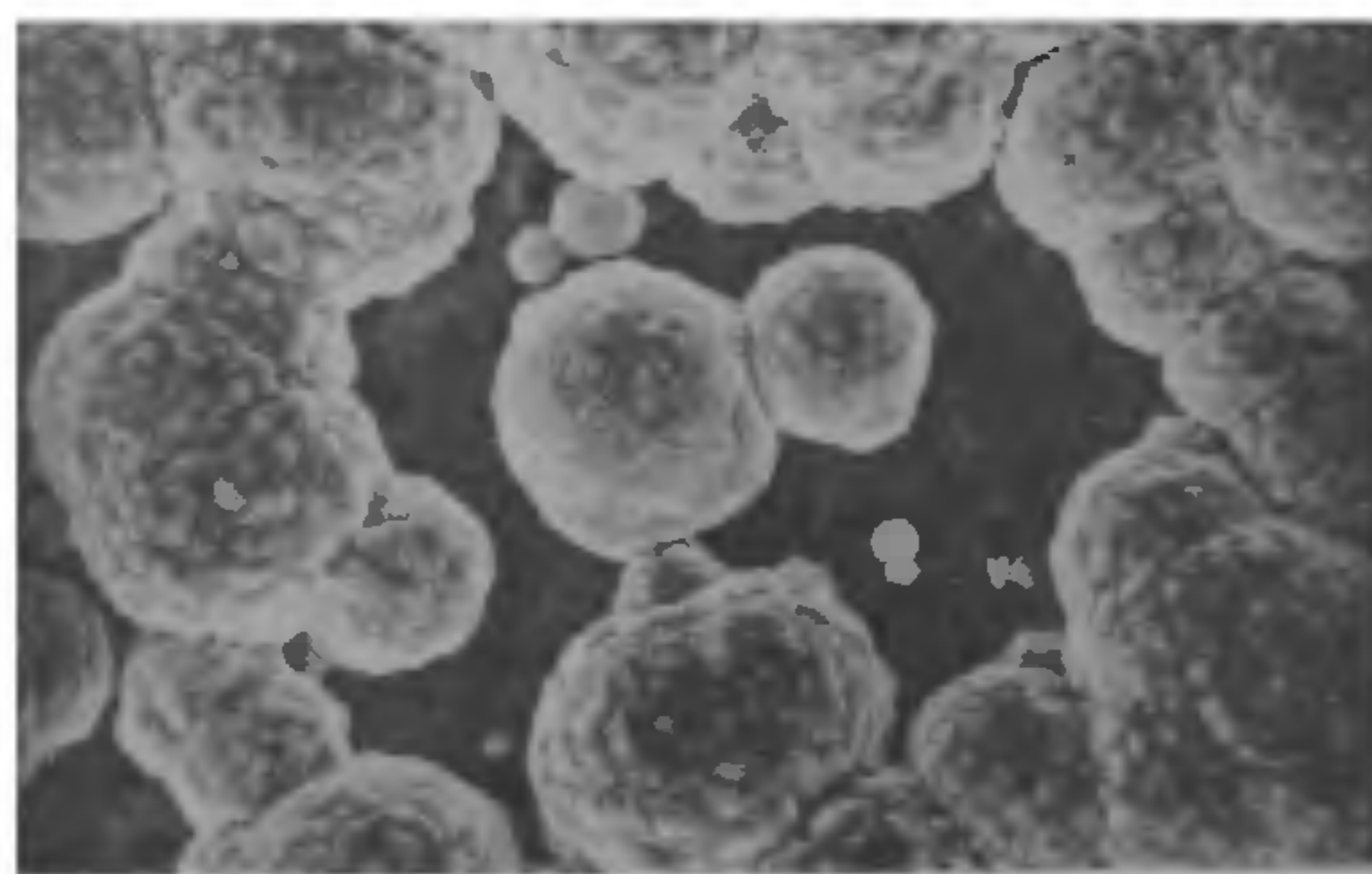


Figure 1. Scanning electron micrograph showing cluster deposit from pure acid copper sulphate bath on  $\text{Cu}_{60}\text{-Zr}_{40}$  metallic glass at  $10 \text{ mA cm}^{-2}$ .