FIG. 3. Polycrystalline deposit when copper is deposited on copper (100) face from acid sulphate bath containing 10^{-4} mol l^{-1} of 2-thiouracil at 10 mA cm^{-2} (magnification 625 ×).

The overpotential value during the deposition in presence of 2-thiouracil was always less than that of the pure solution at the corresponding current density studied. The Tafel relationship holds good at low and moderate concentrations of 2-thiouracil, but at very high concentrations it was not valid. The calculated value of Tafel slope at various concentrations of 2-thiouracil studied was 120 ± 5 mV agreeing with the value determined in the case of pure solution by Bockris *et al.*[7]. A decrease in the value of exchange current density was noticed in the presence of 2-thiouracil.

The above results indicate the remarkable effect of 2-thiouracil on the habit modification of copper electrodeposit. At low concentrations of 2-thiouracil in the bath, the transport mechanism may be due to the formation of 1:1 complex, which may get discharged at a faster rate, compared to the discharge of copper ions in pure solution, resulting in a decrease in overpotential. At higher concentrations, copper mercaptide may be formed as revealed by the disappearance of the absorption peak, characteristic of S–H group in the I.R. spectra of the compound obtained with copper sulphate solution and 2-thiouracil. The copper mercaptide may get adsorbed on the active sites and may hinder growth leading to shortened layers and finally ridges. Finally the copper mercaptide obstructs the incorporation of copper adions and leads to random nucleation resulting in a polycrystalline deposit.

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A CONVENIENT SYNTHESIS OF MELITERNATIN

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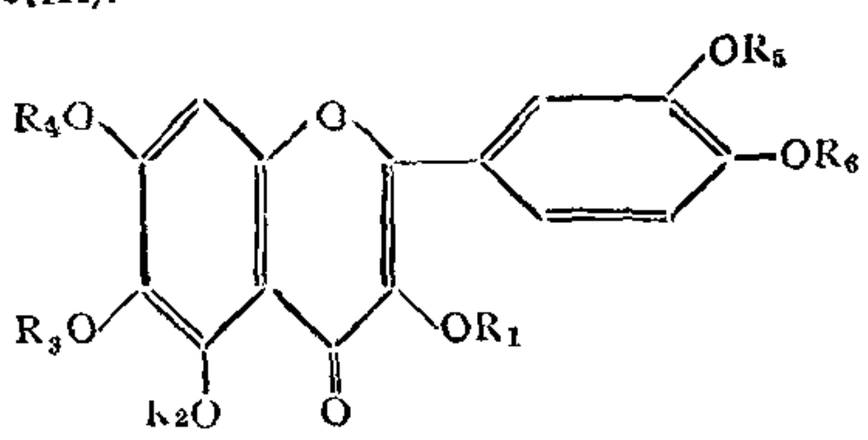
METHYLENATION of 3,6,7,3′,4′-pentahydroxy-5-methoxyflavone(II) obtained by the selective methylation of chelated 5-hydroxyl of 3,5,6,7,3′,4′-hexahydroxyflavone(I), followed by the methylation of the resulting 3-hydroxy-5-methoxy-6, 7, 3′, 4′-dimethylenedioxyflavone (III) gave 3,5-dimethoxy-6,7,3′, 4′-dimethylenedioxyflavone(IV) identical with an authentic sample of meliternatin.

This paper reports an unambiguous and a convenient synthesis of meliternatin isolated from *Melicope ternata*[1,2] and thus provides further confimation of constitution assigned to this compound and its demethylation product[2] which were considered as 3,5-dimethoxy-6,7,3′,4′-dimethyleredioxyflavone(IV) and 3-hydroxy-5-methoxy-6,7,3′,4′-dimethyleredioxyflavore(V). The earlier synthesis of this flavene(IV) reported by Fukui *et al.*[3] was cumbersome and also involved large number of steps with poor yields. The present synthesis consists of two parts: The first part involved the preparation of 3,6,7,3′,4′-pentahydroxy-5-methoxyflavone(II) by the selective methylation[4] of the chelated hydroxyl in quercetagetin(I). As such the hexahydroxyflavone(I) could have been directly methylenated to 3,5-dihydroxy-6,7,3′,4′-dimethylenedioxyflavore(VI) which then on methylation should give 3,5-dimethoxy-6,7,3′,4′-dimethyleredioxyflavone(IV). However, during such a methylenation, the formation of the isomeric 3,7-dihydroxy-5,6,3′,4′-dimethyleredioxyflavore(VII) along with the required flavore(VI) could not be ignored. In order to rule out the possibility of the formation of VII, it was considered necessary to protect this C_5-hydroxyl in I by alkylation before methylenation.

The second part consisted of the methylenation of 3,6,7,3′,4′-pentahydroxy-5-methoxyflavone(II) using methylene iodide and potassium carbonate in acetone and N : N-dimethylformamide mixture to yield a product that was characterised as 3-hydroxy-5-methoxy-6,7,3′,4′-dimethylenedioxyflavone(III) based on the following considerations. The methylenation product (*a*) analysed for $C_{18}H_{12}O_8$, (*b*) gave positive Labat test[5,6], showing the presence of methylenedioxy substituent, (*c*) did not respond to Asahina Inubuse test[7,8] showing the presence of free hydroxyl at C_8, (*d*) on alkali degradation gave piperonylic acid thereby fixing a methylenedioxy group at $C_{3'}$ and $C_{4'}$, (*e*) did not respond to Gibbs test[9,10] showing the absence of a free hydroxyl having an unsubstituted para position and (*f*) on methylation under mild conditions yielded 3,5-dimethoxy-6,7,3′,4′-dimethylenedioxyflavone(IV) identical with the authentic sample of meliternatin in all respects. Since the methylenation product III was different from the demethylation product of meliternatin reported by Briggs *et al.*[2] the constitution of the latter could be indirectly confirmed as 3-methoxy-5-hydroxy-6,7,3′,4′-dimethylenedioxyflavone(V) and not as 3-hydroxy-5-methoxy 6,7,3′,4′-dimethylenedioxyflavone(III).



I, $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$
II, $R_1 = R_3 = R_4 = R_5 = R_6 = H$; $R_2 = CH_3$
III, $R_1 = H$; $R_2 = CH_3$; $R_3R_4 = R_5R_6 = -CH_2-$
IV, $R_1 = R_2 = CH_3$; $R_3R_4 = R_5R_6 = -CH_2-$
V, $R_1 = CH_3$; $R_2 = H$; $R_3R_4 = R_5R_6 = -CH_2-$
VI, $R_1 = R_2 = H$; $R_3R_4 = R_5R_6 = -CH_2-$
VII, $R_1 = R_4 = H$; $R_2R_3 = R_5R_6 = -CH_2-$

Experimental

3-Hydroxy-5-methoxy-6,7,3′,4′-dimethylenedioxyflavone(III)

A mixture of 3,6,7,3′,4′-pentahydroxy-5-methoxyflavone[4](II) (0·17 g), methylene iodide (0·4 ml), anhydrous potassium carbonate (1 g) in N : N-dimethylformamide-acetone mixture (75 ml; 1:9) was refluxed for 40 hr. The inorganic salts were filtered, washed with acetone and the solvent was removed under reduced pressure. The residue thus obtained was treated with water and left overnight. 3-Hydroxy-5-methoxy-6,7,3′,4′-dimethylenedioxyflaovne(III) thus obtained, crystallised from ethyl acetate-petroleum ether as light yellow micro-needles (0·09 g), m.p. 270–271° (Found: C, 60·95; H, 3·75. $C_{18}H_{12}O_8$ requires C, 60·68; H, 3·40%). It gave positive Labat test[5,6] did not respond either to Asahina–Inubuse test[7,8] or to Gibbs test[9,10].

3,5-Dimethoxy-6,7,3′,4′-dimethylenedioxyflavone(IV)

A solution of III (50 mg) in dry acetone (20 ml) was treated with dimethyl sulphate (0·04 ml) and anhydrous potassium carbonate (0·2g) and the resulting reaction mixture was heated under reflux for 12 hr. The inorganic salts were filtered, washed with acetone and the solvent was removed under reduced pressure. The residue, thus obtained, was treated with ice-coldwater and 3,5-dimethoxy-6,7,3′,4′-dimethylenedioxyflavone(IV) thus obtained crystallised from ethyl acetate–petroleum ether as colourless needles (35 mg), m.p. 198° (Found: C, 61·2; H, 3·60. $C_{19}H_{14}O_8$ requires C, 61·62; H, 3·81%) NMR (δ $CDCl_3$), TMS as internal standard); 3·95 (3H, *s*, 1*x*–OCH_3), 3·98 (3H, *s*, 1*x*–OCH_3), 5·95 (2H, *s*, –O–CH_2–O–), 5·98 (2H, *s*,–O–CH_2–O–), 6·88 (1H, *s*, C_8–H), 7·31 (1H, *d*, $J = 9$Hz, $C_{5'}$–H), 7·62 (2H, *m*, $C_{2'}$–H and C_2–H).

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A NOVEL ROUTE TO POLYHALOARYLCHALCONES

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Polyhaloarylchalcones have been prepared from polyhaloarylcopper(I) compounds or the cuprates and cinnamoyl chloride in THF. Their spectral data are presented.