Constituents of the Higher Fungi Part XV. 3-(3,4-Dihydroxyphenyl)-2,7,8-trihydroxydibenzofuran-1,4-dione, a Precursor of Thelephoric Acid from the Fungus *Suillus grevillei* (Klotsch) Sing. [*Boletus elegans* (Schum. per Fries)]

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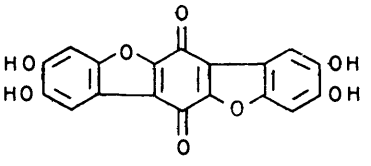
3-(3,4-Dihydroxyphenyl)-2,7,8-trihydroxydibenzofuran-1,4-dione has been isolated from the fungus *Suillus grevillei*. Solutions of this compound are unstable and yield thelephoric acid.

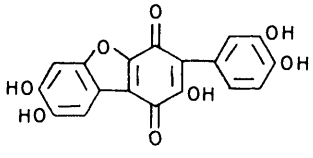
In Part XIV [1] we described the isolation of thelephoric acid (I) and seven new pigments from the larch bolete *Suillus grevillei*. Structures were assigned to three of



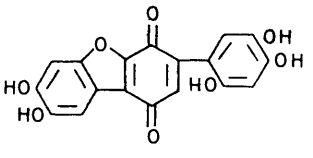
(I)

these compounds (B_1, B_3, and A) and we now report the assignment of the structure (II) to the fourth compound (C_2).

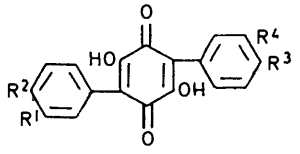
Compound C_2 ($C_{18}H_{10}O_8$, m.p. 300°, M^+ 354) was obtained as dark red needles which form brown solutions in acetone and in alcohols. The presence of five hydroxy-groups was established by the formation of a penta-acetate, and the quinonoid nature of the molecule was shown by its reversible reduction and oxidation with sodium dithionite and air and the formation of a leuco-hepta-acetate. The remaining, unreactive oxygen atom must be involved in an ether bridge since the ^1H n.m.r. spectrum shows absorption only in the aromatic region.



(II)



(III)



(IV) $R^1 = R^2 = R^3 = R^4 = H$
(V) $R^1 = R^4 = H$, $R^2 = R^3 = OH$
(VI) $R^1 = R^2 = R^3 = R^4 = OH$
(VII) $R^1 = R^2 = R^3 = OH$, $R^4 = H$

The molecular formula and polyhydroxylated quinonoid nature of C_2 suggested that it was a hydroxyphenylbenzoquinone. However, the u.v. spectrum of the leuco-acetate ($\lambda_{max.}$ 257, 289, and 312sh nm) differs significantly from those of atromentin leuco-acetate (249 nm) and polyporic acid leuco-acetate (245 nm). Also, C_2 is unstable in alkali; in aqueous sodium hydroxide a blue colouration is produced which fades within 10 s to green and then yellow, and in ammonium hydroxide the transient blue colour fades to a more stable green showing long-wavelength absorption at 658 nm. Polyporic acid (IV) and atromentin (V) are relatively stable in alkali.

Solutions of C_2 are unstable and slowly deposit thelephoric acid (I), identified from its i.r. and u.v. spectra and by the formation of a tetra-acetate and a leuco-hexa-acetate. This instability is particularly marked in acetone solution. The similarity between the chromophores of C_2 and thelephoric acid is illustrated in the Table.

U.v. maxima (nm; log ε in parentheses) of the pigment C_2 and thelephoric acid

Solvent	Pigment C_2	Thelephoric acid
Absolute ethanol	259 (4·39), 301 (4·44), 340infl (4·01), 445 (3·84)	264 (4·27), 305 (4·30), 483 (3·86)
10% EtOH	264 (3·97), 300 (4·00)	271 (3·48), 325 (3·51)
10% EtOH + 2 drops dilute alkali	(NH_4OH) 270 (4·12), 316 (4·11), 658 (3·84)	(NaOH) 274 (3·85), 334 (3·95), 690 (3·59)
0·1N-NaOH	342 (3·96), 394infl (3·77)	344 (4·46), 394infl (4·13), >700
Pyridine	305 (4·24), 331infl (3·78), 446 (3·55)	311 (4·53), 395infl (3·58), 493 (4·05)

Although the formation of the acetate derivatives proves the presence of a quinone ring and five acidic hydroxy-groups it does not distinguish between the two possible structures (II) and (III). Either could conceivably be a direct precursor of thelephoric acid, and structure (II) has recently been suggested as a possible intermediate in the formation of this compound.[2]

Polyporic acid (IV) and atromentin (V) are relatively stable in alkali but the stability of the related polyhydroxylated compounds has not been studied. In order to make a direct comparison with C_2, variegatin (VI) (the hypothetical quinone corresponding to variegatic acid) and leucomelone (VII) have been synthesised. 2,5-Dihydroxy-3,6-bis(hydroxyphenyl)benzoquinones are usually prepared from 2,5-dichlorobenzoquinone by arylation, demethylation, and replacement of halogen by hydroxyl (by treatment with hot sodium hydroxide solution). The synthesis of leucomelone by this sequence has been claimed,[3] and this would imply that the compound is stable in alkaline solution. However, efforts by other workers [4] to prepare leucomelone by reductive demethylation of 3,4,4-trimethoxypolyporic acid and

[1] Part XIV, R. L. Edwards and M. Gill, *J.C.S. Perkin I*, 1973, 1921.

[2] J. Gripenberg, *Tetrahedron Letters*, 1974, 619.

[3] M. Akagi, *J. Pharm. Soc. Japan*, 1942, **62**, 202.

[4] G. J. Benett and N. Uri, *J. Chem. Soc.*, 1962, 2753.

oxidation of the resulting quinol in alkaline solution gave an amorphous product. Also, a demethylation with hydrogen bromide [4] gave a product yielding an unstable acetate of m.p. (196—200°) significantly different from that (226—227°) reported earlier.[3]

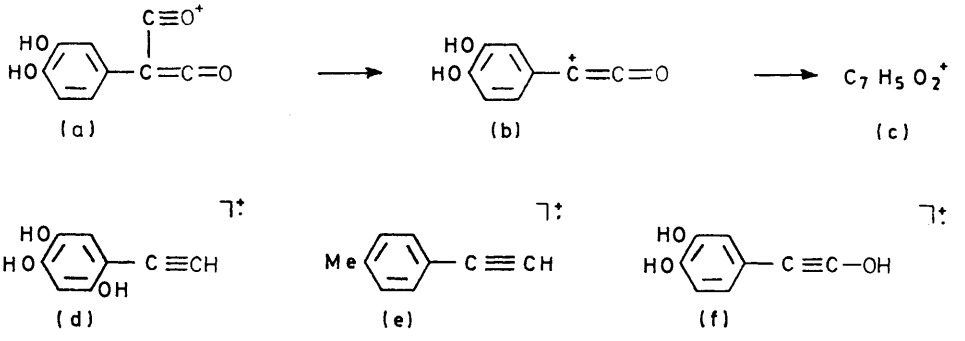
For our synthesis, the acid labile methoxymethyl group was chosen as the hydroxy-protecting group. Diazotised 3,4-bis(methoxymethoxy)aniline was coupled with 2,5-dichlorobenzoquinone to yield the diarylated quinone; this was treated with alkali to remove the halogen and then demethoxymethylated with dilute acid to yield variegatin. Similarly sequential monoarylation of 2,5-dichlorobenzoquinone with diazotised 4-(methoxymethoxy)aniline and then with diazotised 3,4-bis(methoxymethoxy)aniline gave the unsymmetrical diarylated product, which on treatment with alkali and demethoxymethylation gave leucomelone. In both these syntheses the use of alkali after removal of the protecting groups was unnecessary, and during the final demethoxymethylation the crystalline quinones were formed quantitatively during 1 min.

Variegatin (VI) and leucomelone (VII) are both unstable in dilute alkali. In dilute aqueous sodium hydroxide, variegatin produces a blue colouration which fades to yellow within 15 s; in ammonium hydroxide the blue colour fades to a more stable green ($\lambda_{max.}$ 660 nm). Leucomelone produces a blue colouration which fades to a more stable green with both these reagents. Compound C_2 resembles variegatin in these colour reactions.

In the i.r. spectrum C_2 shows strong hydroxy-absorption and complex bands in the carbonyl region. The compound tenaciously holds solvent of crystallisation and removal of this causes marked changes in intensity of bands at 1692, 1650, and 1640 cm^{-1}. In particular that at 1692 cm^{-1} almost disappears after vacuum drying at room temperature for 3 days. Bands near 1640 and 1650 cm^{-1} would be expected for a compound of structure (II), whereas structure (III) would be expected to absorb at 1680 (non-chelated C=O) and 1640 cm^{-1} (C=O in same environment as in thelephoric acid). The possibility that cyclisation might be taking place during drying was ruled out by the preparation of the penta-acetate and the leuco-hepta-acetate from the dried material.

Conclusive proof of structure (II) was obtained from the mass spectrum, which shows features in common with those of variegatin and leucomelone. All three compounds exhibit abundant M^+ and $M^+ - CO$ peaks. Both variegatin and C_2 exhibit a peak at *m/e* 177, which can be represented as the fragment (a) from the 'dihydroxyphenyl' side of the quinone. This would be expected to fragment to yield the ions (b) *m/e* 149 and (c) *m/e* 121; both are found in variegatin and C_2. The fragment of *m/e* 177 is absent from the spectrum of leucomelone but the ions (b) and (c) do appear. Monohydroxy-analogues of these fragments appear only in the spectrum of leucomelone. A compound with structure (III) would be expected to produce the phenylacetylene ion (d) as a major fragment. This type of fragmentation occurs in 2,5-di-(*p*-tolyl)-1,4-benzoquinone, which shows major ions at *m/e* 288 (M^+), 273 ($M - CH_3$), 245 ($M^+ - CH_3 - CO$), and 116 (e). Although a peak is present at *m/e* 150 in the spectrum of C_2, which could correspond to (d), this is weaker than that of the *m/e* 149 ion, and could arise from a simple fragmentation of the benzoquinone nucleus to give (f); this is supported by the presence of this peak in the spectra of variegatin and leucomelone and, in the case of leucomelone, a monohydroxy-analogue at *m/e* 136.

Thelephoric acid is a widespread metabolite of lichens and fungi and the ease with which it can be extracted from some of these sources by either acetone or alcohols has been noted by several workers. Zopf [5] reported a wine-red alcoholic extract from *Thelephora* species and several authors have used acetone as the extracting solvent.[6-8] Asahina and Shibata [8] used acetone to extract thelephoric acid from *Lobaria retigera* and pyridine to extract the same pigment from *Thelephora palmata*. Kögl [9] noted that the compound could only be readily extracted from wet *Thelephora* species by pyridine. The insolubility of thelephoric acid in most solvents and this variation in the ease of extraction from different sources combined with our observation that C_2 readily changes in acetone solution suggests that precursors similar to, or the same as, the compound described in this paper are responsible for the apparent initial solubility of this compound in organic solvents. The initial difficulties in



[5] W. Zopf, *Bot. Z.*, 1889, **8**, 69.
[6] J. Gripenberg, *Acta Chem. Scand.*, 1958, **12**, 1411.
[7] G. Sullivan, L. R. Brady, and V. E. Tyler, *Lloydia*, 1967, **30**, 84.
[8] Y. Asahina and S. Shibata, *Ber.*, 1939, **72**, 1531.
[9] F. Kögl, H. Erxleben, and L. Jänecke, *Annalen*, 1930, **482**, 105.

structure determination and purification also suggest the probable presence of mixtures.[10] It is probable that C_2 is the colouring matter in the cap of *Suillus grevillei* var. badius and is the precursor of the thelephoric acid isolated by us [1] from this species.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus, i.r. spectra on a Perkin-Elmer 237 spectrophotometer, u.v. spectra on a Unicam SP 800 spectrophotometer, ^{1}H n.m.r. spectra on a JEOL JNM-MH-100 spectrometer (tetramethylsilane as internal standard), and mass spectra on an A.E.I. MS9 spectrometer. All thin layer (t.l.c.), preparative layer (p.l.c.), and column chromatography was carried out on Merck Kieselgel $PF_{256+366}$.

Isolation of 3-(3,4-*Dihydroxyphenyl*)-2,7,8-*trihydroxydibenzofuran*-1,4-*dione* (C_2) (II).—The pigment was extracted and isolated as described in Part XIV.[1] Fractions 79—85 deposited dark red *needles* (38 mg), m.p. >300° [Found: C, 60·6; H, 2·9% (after drying under vacuum at room temp. for 48 h); M^+, 354·037624. $C_{18}H_{10}O_8$ requires C, 61·0; H, 2·85%; M, 354·037559]; $\nu_{max.}$ 3490, 3320, 2640, 2530, 1650, and 1640 cm^{-1}; *m/e* 356 (16%), 355 (25), 354 (100), 353 (11), 352 (39), 326 (8), 177 (7), 176 (5), 168 (5), 149 (5), 150 (4), 121 (5), and 120 (5); τ [$(CD_3)_2CO$] 2·2—3·8 (10H).

Thelephoric Acid from Compound C_2.—A solution of the pigment (10 mg) in cold acetone (0·3 ml) was set aside for 3 days. The brown solution slowly deposited crystals of thelephoric acid (5 mg), which were filtered off and washed with acetone and alcohol (Found: M^+, 352·021009. Calc. for $C_{18}H_8O_8$: M, 352·021910); $\nu_{max.}$ 1630 and 1605 cm^{-1}; $\lambda_{max.}$ (pyridine) 493 nm (log ε 4·02).

Acetylation of Compound C_2.—A mixture of C_2 (10 mg), acetic anhydride (0·4 ml), and pyridine (1 drop) was set aside at room temperature. After 48 h the yellow solution was filtered and the filtrate poured into water. Recrystallisation of the solid from benzene–light petroleum (b.p. 80—100°) gave 2,7,8-*triacetoxy*-3-(3,4-*diacetoxyphenyl*)*dibenzofuran*-1,4-*dione* (4 mg) as bright yellow needles, m.p. 137—142° (Found: M^+, 564·093684. $C_{28}H_{20}O_{13}$ requires M, 564·090684); $\nu_{max.}$ ($CHCl_3$) 1780, 1680, 1603, 1583, and 1374 cm^{-1}; *m/e* 564, 522, 480, 438, 396, 354, 337, 326, 177, 149, and 121; $\lambda_{max.}$ 249, 274sh, and 350 nm.

Reductive Acetylation of C_2 *Acetate*.—A mixture of C_2 acetate (5 mg), acetic anhydride (1 ml), anhydrous sodium acetate (0·1 mg), and zinc dust (10 mg) was refluxed for 30 min and then poured into water. 1,2,4,7,8-*Penta-acetoxy*-3-(3,4-*diacetoxyphenyl*)*dibenzofuran* (4·2 mg) was filtered off and crystallised from benzene–light petroleum (b.p. 80—100°) as rods, m.p. 177° (Found: M^+, 650·128480. $C_{32}H_{26}O_{15}$ requires M, 650·127153); $\nu_{max.}$ ($CHCl_3$) 1780, 1509, and 1375 cm^{-1}; $\lambda_{max.}$ 227, 257, 289, and 310sh nm (log ε 4·56, 4·18, 4·37, and 4·01); *m/e* 650, 608, 566, 524, 482, 440, 398, 356, 337, 326, 177, and 149.

3,4-*Bis*(*methoxymethoxy*)-1-*nitrobenzene*.—A mixture of 4-nitrocatechol (103 g), chloromethyl methyl ether (150 g), and anhydrous potassium carbonate (360 g) in anhydrous acetone (1·2 l) was stirred and refluxed for 48 h. The mixture was filtered, the residue was well washed with acetone, and the filtrate was evaporated under reduced pressure. A solution of the oily residue in ether was shaken with aqueous sodium hydroxide (3 × 50 ml; 2N), then water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from aqueous ethanol and recrystallisation from methanol gave 3,4-*bis*(*methoxymethoxy*)-1-*nitrobenzene* (126 g) as pale yellow needles, m.p. 59—63° (Found: C, 49·5; H, 5·4; N, 5·8. $C_{10}H_{13}NO_6$ requires C, 49·4; H, 5·35; N, 5·8%).

3,4-*Bis*(*methoxymethoxy*)*aniline*.—A solution of 3,4-bis(methoxymethoxy)-1-nitrobenzene (146 g) in ethanol (600 ml) was added dropwise to a stirred suspension of palladised charcoal (3 g; 10%) in aqueous sodium borohydride (55 g in 1500 ml) cooled to 5°. Nitrogen was passed through the mixture during the addition. Stirring was continued for 1 h and after filtration the alcohol was evaporated off under reduced pressure. The mixture was acidified with acetic acid and extracted with ether, and the extract washed with cold dilute hydrochloric acid. The base was liberated with alkali and re-extracted into ether. Evaporation, and distillation of the product *in vacuo* gave the *aniline* (82 g), b.p. 146—148° at 0·7 mmHg. Crystallisation from cyclohexane gave the needles, m.p. 52—56° (Found: C, 56·5; H, 7·0; N, 6·5. $C_{10}H_5NO_4$ requires C, 56·3; H, 7·0; N, 6·6%).

3-[3,4-*Bis*(*methoxymethoxy*)*phenyl*]-2,5-*dichloro*-1,4-*benzoquinone*.—Sodium nitrite (2·3 g) in water (10 ml) was added dropwise at 5° to a solution of 3,4-bis(methoxymethoxy)-aniline (6 g, 0·03 mol) in concentrated hydrochloric acid–water (1 : 1; 14 ml). Sodium acetate (7 g) was added and the mixture poured into a solution of 2,5-dichlorobenzoquinone (5·3 g, 0·03 mol) in ethanol (250 ml) and ether (250 ml) at 10°. The dark red solution was set aside overnight and then evaporated to low bulk under reduced pressure. The mixture was extracted with ether, the extract evaporated, and the residue adsorbed on silica gel (20 g) from acetone. The dry gel was placed on a column of silica gel (70 × 4 cm), which was developed with benzene–acetic acid (95 : 5). The product from the first intense red band to be eluted yielded red *plates* (620 mg), m.p. 130—132° (from methanol) (Found: C, 51·4; H, 3·9; Cl, 19·1. $C_{16}H_{14}Cl_2O_8$ requires C, 51·5; H, 3·75; Cl, 19·0%); $\nu_{max.}$ 1677, 1667, and 1600 cm^{-1}.

The product from the second red band gave 3,6-*di*-[3,4-*bis*(*methoxymethoxy*)*phenyl*]2,5-*dichloro*-1,4-*benzoquinone* (155 mg) as bronze plates (from ethanol), m.p. 163—165° (Found: C, 54·7; H, 4·4; Cl, 12·4. $C_{26}H_{26}Cl_2O_{10}$ requires C, 54·8; H, 4·6; Cl, 12·5%); $\nu_{max.}$ 1674 and 1601 cm^{-1}.

Similarly prepared from 2,5-dichlorobenzoquinone (19·5 g) and diazotised 4-methoxymethoxyphenylaniline (15·3 g) was 2,5-*dichloro*-3-[4-(*methoxymethoxy*)*phenyl*]-1,4-*benzoquinone* (7·2 g) as orange-red rods (from ethanol), m.p. 110—112° (Found: C, 54·0; H, 3·4; Cl, 22·6. $C_{14}H_{10}Cl_2O_4$ requires C, 53·7; H, 3·2; Cl, 22·7%); $\nu_{max.}$ 1672, 1665, and 1604 cm^{-1}.

3-[3,4-*Bis*(*methoxymethoxy*)*phenyl*]-2,5-*dichloro*-6-[4-(*methoxymethoxy*)-*phenyl*]-1,4-*benzoquinone*.— 3,4-Bis(methoxymethoxy)aniline (9·8 g) in hydrochloric acid (32 ml; 50%) was diazotised with sodium nitrite (6 g) in water (30 ml) at 5°. Sodium acetate (20 g) was added and the mixture poured into a solution of 2,5-dichloro-3-[4-(methoxymethoxy)phenyl]-1,4-benzoquinone (6·26 g) in ethanol (600 ml) and ether (180 ml) at 10°. The mixture was stirred for 3 h during which time the solution became dark brown and deposited a red solid. Crystallisation from acetic acid yielded the product (1·18 g) as bronze *plates*, m.p. 147—150° (Found: C, 56·7; H, 4·3; Cl, 14·0. $C_{24}H_{22}Cl_2O_8$ requires C, 56·6; H, 4·3; Cl, 13·95%); $\nu_{max.}$ 1676, 1603, 1580, and 1504 cm^{-1}.

3,6-*Di*-[3,4-*bis*(*methoxymethoxy*)*phenyl*]-2,5-*dihydroxy*-1,4-*benzoquinone*.—A suspension of 3,6-di-[3,4-bis(methoxymethoxy)phenyl]-2,5-dichloro-1,4-benzoquinone (100 mg) in

[10] G. Read and L. C. Vining, *Canad. J. Chem.*, 1959, **37**, 1442.

methanol (1·5 ml) and aqueous sodium hydroxide (1·5 ml; 2N) was warmed on a water-bath for 30 min. Acidification of the cold purple solution gave a brown precipitate which was filtered off and crystallised from dioxan to yield the product (70 mg) as yellow *needles*, m.p. 149—153° (Found: C, 58·4; H, 5·2. $C_{26}H_{28}O_{12}$ requires C, 58·65; H, 5·3%); $\nu_{max.}$ 1646, 1626, 1599, 1580, and 1513 cm^{-1}.

3-[3,4-*Bis*(*methoxymethoxy*)*phenyl*]-2,5-*dihydroxy*-6-[4-(*methoxymethoxy*)*phenyl*]-1,4-*benzoquinone*, similarly prepared from the corresponding dichloro-compound, was obtained as orange needles (from dioxan), m.p. 120° (Found: C, 60·8; H, 5·0. $C_{24}H_{24}O_{10}$ requires C, 61·0; H, 5·1%); $\nu_{max.}$ 1630, 1619, 1609, and 1510 cm^{-1}.

Variegatin (VI) *and Leucomelone* (VII).—A mixture of 2,5-dihydroxy-3,6-bis(methoxymethoxy)phenyl-1,4-benzoquinone (35 mg), acetic acid (1·5 ml), and sulphuric acid (1 drop; 2N) was boiled for 1 min. The solution deposited a crystalline brown solid. Recrystallisation from pyridine gave 2,5-bis-(3,4-*dihydroxyphenyl*)-3,6-*dihydroxy*-1,4-*benzoquinone* (variegatin) (19 mg) as red rods which turned brown on heating *in vacuo*; m.p. >320° (Found: C, 60·7; H, 3·55. $C_{18}H_{12}O_8$ requires C, 60·7; H, 3·4%); $\nu_{max.}$ 3490, 1640sh, 1629, 1620, 1605, and 1514 cm^{-1}; $\lambda_{max.}$ 216sh, 270, and 282 nm (log ε 4·31, 4·16, and 4·21); $\lambda_{max.}$ (10% ethanol) 285 and 354sh nm (log ε 3·85 and 2·90); $\lambda_{max.}$ (10% ethanol + 2 drops 2N-NH_4OH) 250sh, 331, and 660 nm (log ε 3·87, 3·94, and 3·83); $\lambda_{max.}$ (0·1N-NaOH) 250sh, 332, and 384 nm (log ε 4·42, 4·43, and 4·32); *m/e* 356 (100%), 328 (75), 255 (20), 177 (20), 161 (49), 150 (80), 149 (49), 123 (64), 122 (44), and 121 (72).

Similarly, hydrolysis of 3-[3,4-bis(methoxymethoxy)-phenyl]-2,5-dihydroxy-6-[4-(methoxymethoxy)phenyl]-1,4-benzoquinone (100 mg) gave leucomelone (36 mg) as orange plates (from dioxan), m.p. >320° (Found: C, 63·3; H, 3·4. Calc. for $C_{18}H_{12}O_7$: C, 63·55; H, 3·55%); $\nu_{max.}$ 3400, 1637sh, 1625, 1602, and 1510 cm^{-1}; $\lambda_{max.}$ 271, 282, and 386 nm (log ε 4·42, 4·41, and 3·29); $\lambda_{max.}$ (10% ethanol) 281 and 345sh nm (log ε 4·19 and 3·26); $\lambda_{max.}$ (10% ethanol + 2 drops 2N-NH_4OH) 295 and 654 nm (log ε 4·14 and 4·79); $\lambda_{max.}$ (0·1N-NaOH) 260, 326, 382, and 676 nm (log ε 4·06, 4·07, 3·82, and 3·33); *m/e* 340 (100%), 312 (47), 161 (43), 150 (40), 149 (19), 145 (22), 134 (43), 133 (26), 123 (47), 122 (22), 121 (39), and 105 (41).

Leucomelone Penta-acetate and Variegatin Hexa-acetate.—A mixture of leucomelone (50 mg), acetic anhydride (0·4 ml), and sulphuric acid (1 drop) was heated on a water-bath for 15 min, cooled, and poured into water. The product (42 mg) crystallised from acetic acid to yield lemon-yellow needles of leucomelone penta-acetate, m.p. 179—182° (decomp.) (lit.,[4] 196—200°; lit.,[3] 226—227°) (Found: C, 61·3; H, 4·3. Calc. for $C_{28}H_{22}O_{12}$: C, 61·1; H, 4·0%); $\nu_{max.}$ 1773, 1671, 1613, and 1499 cm^{-1}.

Similarly, variegatin gave *variegatin hexa-acetate* as yellow needles (from acetic anhydride), m.p. 184—186° (decomp.) (Found: C, 58·8; H, 4·0. $C_{30}H_{24}O_{14}$ requires C, 59·2; H, 3·9%); $\nu_{max.}$ 1780, 1680, 1620, 1610, and 1503 cm^{-1}.

Leucomelone Hepta-acetate and Variegatin Octa-acetate.—A mixture of leucomelone (25 mg), acetic anhydride (3 ml), anhydrous sodium acetate (10 mg), and zinc dust (50 mg) was heated under reflux for 10 min. The mixture was cooled, filtered, and poured into water. Crystallisation of the solid from ethanol gave needles of leucomelone hepta-acetate (19 mg), m.p. 218° (after softening at 205°) (lit.,[3] 204—205°) (Found: C, 60·1; H, 4·3. Calc. for $C_{32}H_{28}O_{14}$: C, 60·4; H, 4·4%); $\nu_{max.}$ 1775 cm^{-1}.

Similarly, variegatin gave *variegatin octa-acetate* as needles (from acetic acid), m.p. 242—244° (Found: C, 58·6; H, 4·25. $C_{34}H_{30}O_{16}$ requires C, 58·8; H, 4·3%); $\nu_{max.}$ 1775 cm^{-1}.

We thank the S.R.C. for a research grant (to M. G.).

[4/1886 *Received*, 16*th September*, 1974]