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A New Synthesis of Xanthones. 2,4,7-Trichloronorlichexanthone and 4,5,7-Trichloronorlichexanthone, Two New Lichen Xanthones

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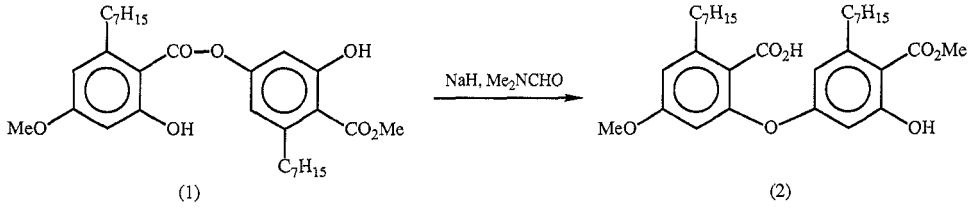
Abstract

A new synthetic route to norlichexanthone (1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one) derivatives has been developed by using a Smiles rearrangement of an appropriately substituted depside in the key step. 2,4,7-Trichloronorlichexanthone (22) and 4,5,7-trichloronorlichexanthone (29) have been prepared by this method. The former xanthone (22) was shown to be a constituent of the lichens *Lecanora sulphurata* and *L. flavo-pallescens* and the latter (29) a constituent of *Micarea austroternaria* var. *isabellina*.

Introduction

A number of synthetic applications have derived from the key discovery that *para*-depsides such as methyl prasinate (1) could be readily converted into the isomeric 2-phenoxybenzoic acid (2) through an intramolecular Smiles rearrangement under mild conditions (Scheme 1).[1] Thus, the Smiles rearrangement of a precursor *para*-depside was employed in a biomimetic-type synthesis of the lichen dibenzofurans schizopeltic acid and pannaric acid,[2] while a similar rearrangement of a precursor *meta*-depside was employed in a synthesis of the the lichen depsidones divaronic acid and stenosporonic acid[3] as well as the diphenyl ether, epiphorellic acid 1.[4]



(1) (2)

Scheme 1

[1] Elix, J. A., Jones, A. J., Lajide, L., Coppins, B. J., and James, P. W., *Aust. J. Chem.*, 1984, **37**, 2349.
[2] Elix, J. A., and Parker, J. L., *Aust. J. Chem.*, 1987, **40**, 187.
[3] Elix, J. A., Jenie, U. A., and Parker, J. L., *Aust. J. Chem.*, 1987, **40**, 1451.
[4] Elix, J. A., and Jenie, U. A., *Aust. J. Chem.*, 1989, **42**, 987.

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This rearrangement appeared to provide a convenient route to highly substituted 2-phenoxybenzoic acids, already known as appropriate intermediates in the synthesis of 8-methyl-9*H*-xanthen-9-ones.[5] Hence, the viability and synthetic potential of the Smiles rearrangement of appropriately substituted depsides was investigated as a key step in the synthesis of natural lichen xanthones. The mononuclear precursors were prepared from ethyl orsellinate and 2,4,6-trihydroxybenzoic acid by well established procedures.[5–9]

Synthesis of 7-Chloro-8-methyl-9*H*-xanthen-9-ones

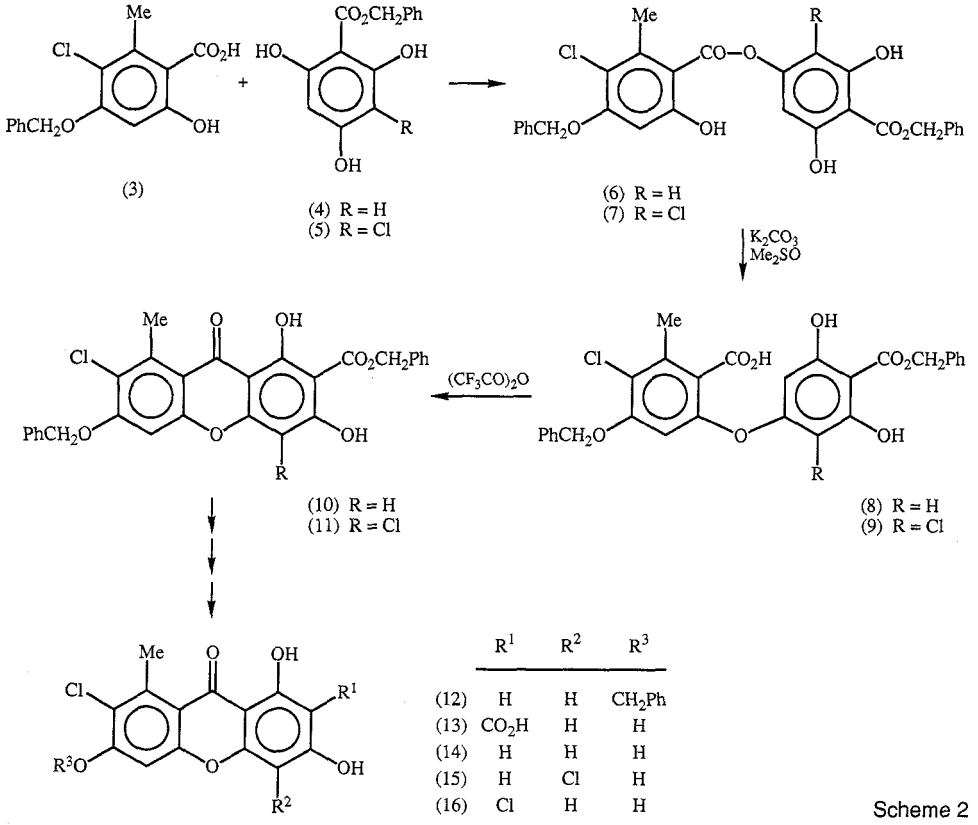
The condensation of 4-benzyloxy-3-chloro-6-hydroxy-2-methylbenzoic acid (3) with benzyl 2,4,6-trihydroxybenzoate (4) and benzyl 3-chloro-2,4,6-trihydroxybenzoate (5) in the presence of trifluoroacetic anhydride afforded the corresponding depside esters (6) and (7) in reasonable yield. Regioselective esterification of the phenolic esters (4) and (5) occurred at the less hindered, non- or weakly intramolecularly hydrogen-bonded hydroxy group of each ester. The structure of the depside esters was confirmed by microanalytical evidence as well as spectroscopic data. In particular, the ^{1}H n.m.r. spectrum of (6) revealed a singlet peak at δ 6·35 (2H), due to H3 and H5, and a singlet peak at 9·90 (2H) due to the hydroxy groups at positions 2 and 6, so confirming the symmetry of the B-ring.

Treatment of the depsides (6) and (7) with anhydrous potassium carbonate in dimethyl sulfoxide solution at room temperature effected the Smiles rearrangement and afforded the corresponding 2-phenoxybenzoic acids (8) and (9) in high yield. Although these proved rather difficult to purify, treatment of the crude material with trifluoroacetic anhydride led to the corresponding xanthones, benzyl 6-benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9*H*-xanthen-9-one-2-carboxylate (10) and the 4,7-dichloro derivative (11) respectively (Scheme 2).

The treatment of the benzyl ester (10) with potassium hydroxide in aqueous dimethyl sulfoxide solution at 100–110° effected hydrolysis and concomitant decarboxylation to afford 6-benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9*H*-xanthen-9-one (12). Subsequent debenzylation of (12) by treatment with boron trichloride gave 7-chloronorlichexanthone (14), identical with authentic material.[10] Alternatively, the benzyl ester (10) was first debenzylated by reaction with boron trichloride, and the carboxylic acid (13) so produced was subsequently decarboxylated by treatment with hot potassium hydroxide to give (14).

The chlorination of 7-chloronorlichexanthone (14) with *N*-chlorosuccinimide and a trace of toluene-4-sulfonic acid was also investigated. Here the major product was the 4,7-dichloro compound (15), while the minor product was 2,7-dichloronorlichexanthone (16). The respective ^{1}H n.m.r. spectra confirmed that in both cases chlorination occurred in the B-ring (each contained a low-field

[5] Fitzpatrick, L., Sala, T., and Sargent, M. V., *J. Chem. Soc., Perkin Trans. 1*, 1980, 85.
[6] Elix, J. A., Musidlak, H. W., Sala, T., and Sargent, M. V., *Aust. J. Chem.*, 1978, **31**, 145.
[7] Sundholm, E. G., *Tetrahedron*, 1978, **34**, 577.
[8] Sundholm, E. G., *Acta Univ. Ups. Abstr. Uppsala Diss. Fac. Sci.*, 1979, **526**, 1.
[9] Sundholm, E. G., *Acta Chem. Scand., Ser. B*, 1979, **33**, 475.
[10] Huneck, S., and Höfle, G., *Tetrahedron*, 1978, **34**, 2491.



	R^1	R^2	R^3
(12)	H	H	CH_2Ph
(13)	CO_2H	H	H
(14)	H	H	H
(15)	H	Cl	H
(16)	Cl	H	H

Scheme 2

aromatic proton at δ 6·97 and 6·91 respectively). Moreover, the structure of 4,7-dichlorononorlichexanthone (15) was established by the unambiguous synthesis in the following manner. Thus, treatment of the ester (11) with potassium hydroxide in aqueous dimethyl sulfoxide solution at reflux effected ester hydrolsis, decarboxylation, and debenzylation of the 6-benzyloxy group to afford (15) directly.

Synthesis of 3-Methoxy-8-methyl-9*H*-xanthen-9-ones

A number of naturally occurring, chlorine-containing lichen xanthones possess a 3-methoxy substituent,[11-13] so the utility of the above synthesis and intermediates as a route to these compounds was investigated (Scheme 3). When the benzyl ester (11) was treated with potassium hydroxide in aqueous dimethyl sulfoxide solution at 120–135°, ester hydrolysis and decarboxylation occurred to afford 6-benzyloxy-4,7-dichloro-1,3-dihydroxy-8-methyl-9*H*-xanthen-9-one (17). This compound was selectively methylated by reaction with dimethyl sulfate and anhydrous potassium carbonate to give

[11] Culberson, C. F., 'Chemical and Botanical Guide to Lichen Products' (University of North Carolina Press: Chapel Hill 1969).
[12] Culberson, C. F., Supplement to 'Chemical and Botanical Guide to Lichen Products', *Bryologist*, 1970, **73**, 177.
[13] Elix, J. A., Whitton, A. A., and Sargent, M. V., *Fortschr. Chem. Org. Naturst.*, 1984, **45**, 104.

the corresponding 3-methoxy compound (18). The strongly intramolecularly hydrogen-bonded 1-hydroxy group was not reactive under these conditions. Subsequent debenzylation of (18) with boron trichloride led smoothly to 4,7-dichloro-1,6-dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (19) in high yield. Chlorination of the xanthone (19) with sulfuryl chloride led to the formation of two isomeric trichloroxanthones, 2,4,7-trichloro-1,6-dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (20), the major product, and 4,5,7-trichloro-1,6-dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (21), the minor product. The structure of these two isomers followed from that of the synthetic precursor (19) and from their respective ^{1}H n.m.r. spectra, that of the former exhibiting a low-field singlet signal in the aromatic region (δ 7·05) and that of the latter a high-field signal (6·50) consistent with these formulations. 4,5,7-Trichloro-1,6-dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (21) (*O*-methylasemone) has recently been reported to occur in the lichen *Lecidella buelliastrum* (Müll. Arg.) Knoph & Rambold.[14]

These syntheses established the overall utility of this approach for the preparation of substituted 3-methoxy-8-methyl-9*H*-xanthen-9-ones.

Synthesis and Natural Occurrence of 4,5,7-Trichloronorlichexanthone (29)

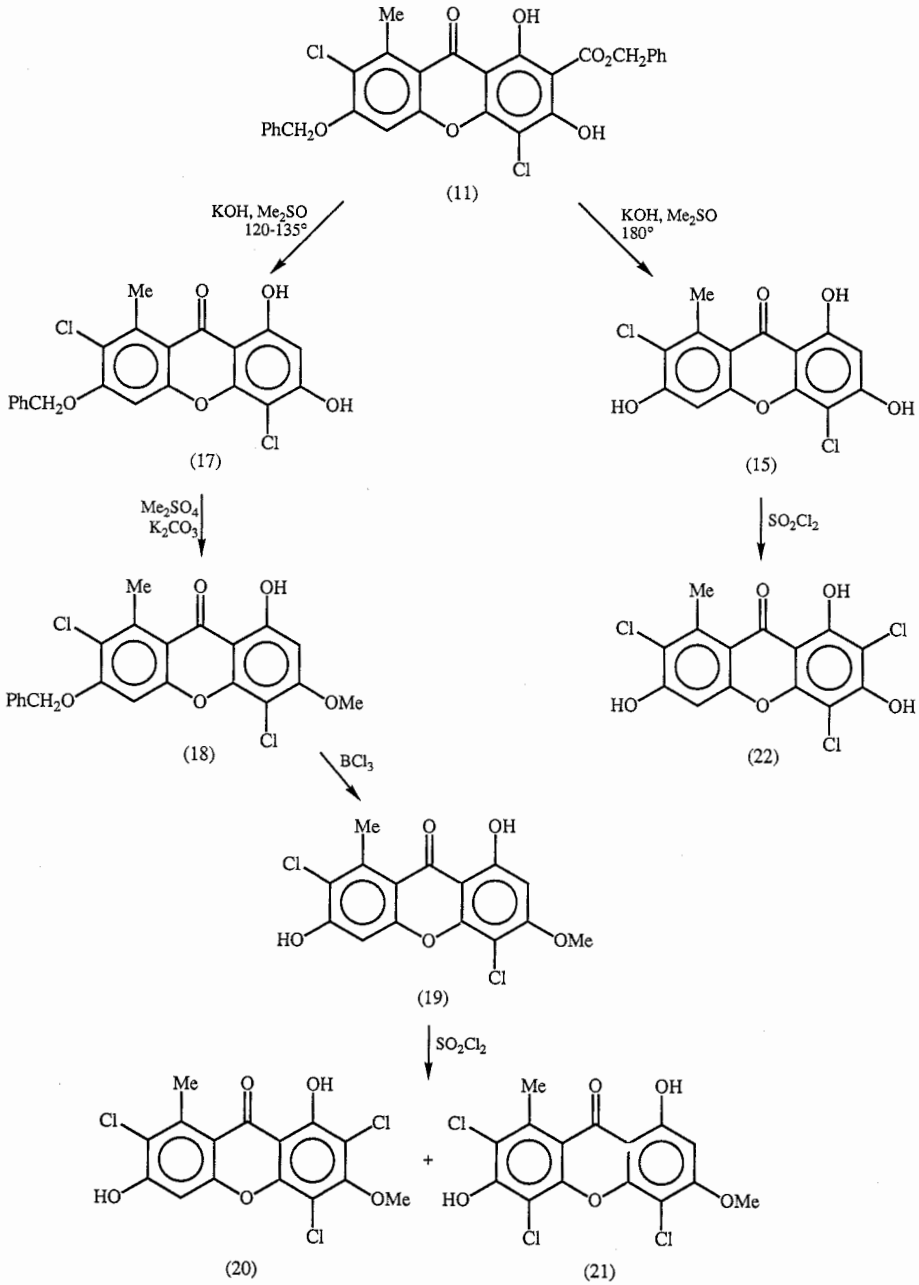
By using the appropriately substituted benzoic acid, the corresponding 6-methoxy-8-methyl-9*H*-xanthen-9-ones can also be synthesized (Scheme 4). Thus, starting from 3,5-dichloro-2-hydroxy-4-methoxy-6-methylbenzoic acid (23) and benzyl 3-chloro-2,4,6-trihydroxybenzoate (5) we proceeded in a similar manner via the depside ester (24) and the 2-phenoxybenzoic acid (25) to the xanthone ester (26). Debenzylation of (26) by treatment with boron trichloride gave the corresponding acid (27). When the acid (27) was treated with potassium hydroxide in aqueous dimethyl sulfoxide solution at 120–135°, decarboxylation occurred to afford 4,5,7-trichloro-1,3-dihydroxy-6-methoxy-8-methyl-9*H*-xanthen-9-one (28) together with some of the corresponding demethylated derivative 4,5,7-trichloronorlichexanthone (29). The latter compound was shown to be a minor constituent of the Tasmanian lichen *Micarea austroternaria* var. *isabellina* Coppins & Kantvilas by comparative chromatography (t.l.c., h.p.l.c.) (see Table 1). This is the first reported natural occurrence of 4,5,7-trichloronorlichexanthone (29).

Synthesis and Natural Occurrence of 2,4,7-Trichloronorlichexanthone (22)

The synthesis of this compound was achieved by direct chlorination of 4,7-dichloronorlichexanthone (15), prepared above, by treatment with sulfuryl chloride at room temperature (Scheme 3). The structure of the 2,4,7-trichloro compound (22) so formed was confirmed by spectroscopic data. The molecular formula was established by mass spectroscopy as $C_{14}H_{11}Cl_3O_5$ by high-resolution mass measurement on the molecular ion. Further, the ^{1}H n.m.r. spectrum exhibited a low-field aromatic singlet at δ 6·96, typical of an A-ring proton (in this case H 5).[13]

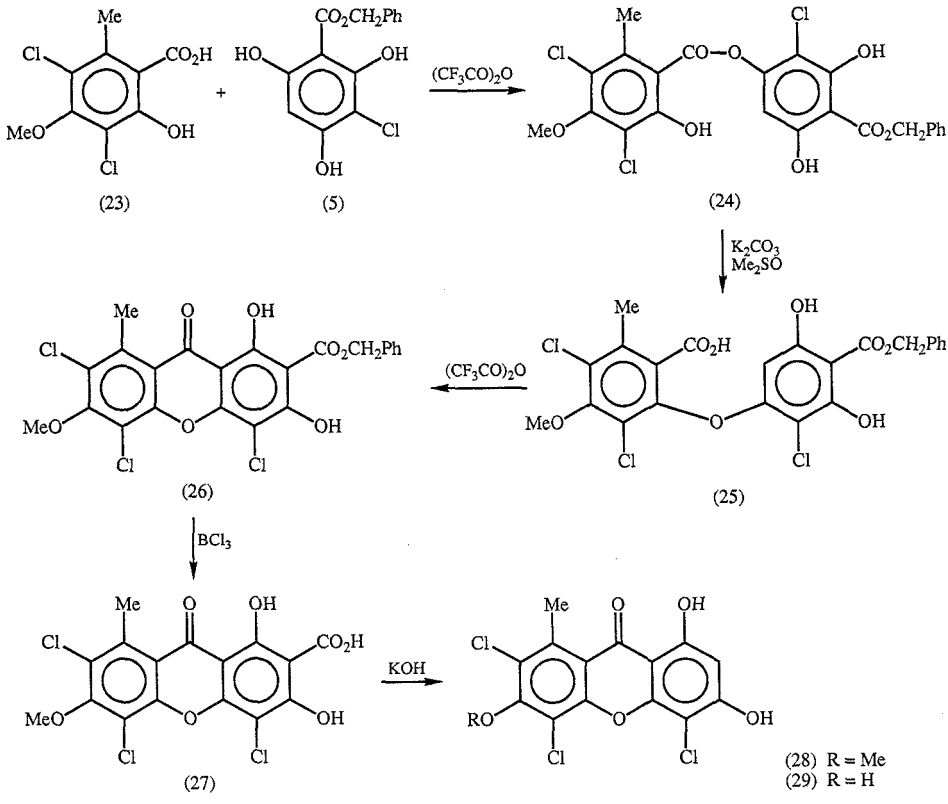
[14] Rambold, G., *Bibl. Lichenol.*, 1989, **34**, 1.

The synthetic sample of 2,4,7-trichloronorlichexanthone (22) proved to be identical (t.l.c., h.p.l.c., m.s.) with a minor metabolite present in the lichens *Lecanora sulphurata* (Ach.) Nyl. and *L. flavo-pallescens* Nyl. The isomeric 2,5,7-trichloronorlichexanthone (isoarthothelin) (30) was previously reported to be the major trichloroxanthone present in these two species[8,9,15] but we have



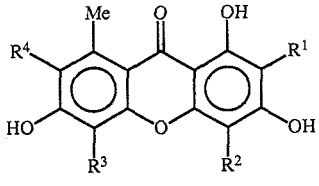
Scheme 3

[15] Santesson, J., *Ark. Kemi*, 1969, **31**, 57.



Scheme 4

recently shown this not to be so.[16] Comparative chromatography (t.l.c., h.p.l.c.) here confirmed the presence of significant quantities of arthothelin (31)[5,7] and 2,4,7-trichoronorlichexanthone (22) in *L. sulphurata* together with traces of isoarthothelin (30) (Table 1). Thiophanic acid (32) was the major constituent of *L. sulphurata.* In addition to (32), the New Zealand species *L. flavo-pallescens* contained significant quantities of 2,4,7-trichoronorlichexanthone (22), arthothelin (31) and 4,5-dichloronorlichexanthone (33). The fact that resolution of 2,4,7-trichoronorlichexanthone (22) and isoarthothelin (30) by thin-layer chromatography (t.l.c.) was very difficult may account for the previous confusion of these two compounds.[8,9,15] These isomers are readily resolved by high-performance liquid chromatography (h.p.l.c.) as shown in Table 1. This is the first reported natural occurrence of 2,4,7-trichloronorlichexanthone (22).



	R^1	R^2	R^3	R^4
(30)	Cl	H	Cl	Cl
(31)	Cl	Cl	Cl	H
(32)	Cl	Cl	Cl	Cl
(33)	H	Cl	Cl	H

[16] Elix, J. A., Jiang H., and Portelli, V. J., *Aust. J. Chem.*, 1990, **43**, 1291.

Table 1. Resolution of isomers by h.p.l.c.

Compound	Approximate composition (%) *Micarea austroternaria*	*Lecanora sulphurata*	*Lecanora flavo-pallescens*	H.p.l.c. R_t (min)
4,5,7-Trichloronorlichexanthone (29)	9·1	—	—	6·95
2,4,7-Trichloronorlichexanthone (22)	—	1·3	4·3	6·90
Isoarthothelin (30)	—	0·8	—	6·60
Arthothelin (31)	9·3	3·4	25·0	6·13
Thiophanic acid (32)	70·2	83·3	60·9	8·34
4,5-Dichloronorlichexanthone (33)	2·6	—	6·1	5·20
Atranorin	—	9·5	—	7·42
Unknowns	8·6	1·7	3·7	—

Experimental

The general experimental details have been described previously.[16]

Ethyl 4-Benzyloxy-3-chloro-6-hydroxy-2-methylbenzoate

A solution of ethyl 4-benzyloxy-2-hydroxy-6-methylbenzoate[17] (4 g, 14 mmol) in anhydrous diethyl ether (59 ml) was treated with a solution of sulfuryl chloride (1·89 g, 14 mmol) in anhydrous ether (30 ml), and stirred at 17° for 17 h. Evaporation of the solvent under reduced pressure gave the crude product (3·9 g, 87%) which was crystallized from dichloromethane to give *ethyl 4-benzyloxy-3-chloro-6-hydroxy-2-methylbenzoate* as colourless prisms, m.p. 112–113° (Found: C, 63·6; H, 5·5; Cl, 10·9. $C_{17}H_{17}ClO_4$ requires C, 63·7; H, 5·3; Cl, 11·1%). ^{1}H n.m.r. ($CDCl_3$) δ 1·40, t, J 7 Hz, OCH_2**Me**; 2·65, s, ArMe; 4·35, q, J 7 Hz, OC**H**$_2$Me; 5·13, s, $ArCH_2O$; 6·41, s, ArH; 7·40, m, Ph. Mass spectrum *m/z* 322 (2·5%), 320 (M, 7·4), 91 (100).

4-Benzyloxy-3-chloro-6-hydroxy-2-methylbenzoic Acid (3)

A mixture of ethyl 4-benzyloxy-3-chloro-6-hydroxy-2-methylbenzoate (1·90 g, 5·9 mmol), dimethyl sulfoxide (29 ml), potassium hydroxide (1·3 g) and water (6 ml) was stirred and heated at 98° for 4 h. The mixture was then cooled, diluted with water and extracted with ether to remove any unchanged starting material. The basic aqueous layer was poured into cold, dilute hydrochloric acid, extracted with ether, and the ethereal extract washed with water, with saturated brine, and dried ($MgSO_4$). After removal of solvent, the residue was crystallized from cyclohexane to give *4-benzyloxy-3-chloro-6-hydroxy-2-methylbenzoic acid* (3) (0·89 g, 51%) as colourless crystals, m.p. 221–222° (Found: C, 61·3; H, 4·3; Cl, 12·5. $C_{15}H_{13}ClO_4$ requires C, 61·6; H, 4·5; Cl, 12·1%). ^{1}H n.m.r. ($CDCl_3$) δ 2·71, s, ArMe; 5·22, s, OCH_2; 6·55, 1H, s, ArH; 7·42, 5H, m, Ph. Mass spectrum *m/z* 294 (0·4%), 292 (M, 1·3), 91 (100).

Benzyl 2,4,6-Trihydroxybenzoate (4)

A mixture of 2,4,6-trihydroxybenzoic acid (10 g, 58·8 mmol), benzyl bromide (5 ml, 39·4 mmol) and potassium hydrogen carbonate (10 g) in dimethylacetamide (100 ml) was stirred at room temperature overnight. The reaction mixture was then diluted with ethyl acetate (400 ml) and water (400 ml). The organic layer was separated, washed with water and

[17] Aghoramurthy, K., and Seshadri, T. R., *Proc. Indian Acad. Sci., Sect. A*, 1952, **35**, 327.

saturated brine, and dried ($MgSO_4$). The solvent was evaporated and the residue crystallized from ethanol/water to give *benzyl 2,4,6-trihydroxybenzoate* (4) (7·6 g, 74%) as colourless crystals, m.p. 127–128° (Found: C, 60·4; H, 5·0. $C_{14}H_{12}O_5$ requires C, 60·4; H, 5·1%). ^1H n.m.r. ($CDCl_3$) δ 5·58, s, OCH_2; 5·95, s, ArH; 7·50, m, Ph; 9·43, s, OH; 10·03, s, 2×OH. Mass spectrum *m/z* 260 (M, 3·1%), 91 (100).

Benzyl 3-Chloro-2,4,6-trihydroxybenzoate (5)

A solution of sulfuryl chloride (2·7 g, 20 mmol) in anhydrous ether (40 ml) was added dropwise to a solution of benzyl 2,4,6-trihydroxybenzoate (4) (5·2 g, 20 mmol) in anhydrous diethyl ether (80 ml), and the mixture stirred at room temperature for 17 h. Evaporation of the solvent under reduced pressure then gave the crude product which was purified by column chromatography (silica gel) by using 10–14% ethyl acetate/light petroleum as eluent. The major band gave *benzyl 3-chloro-2,4,6-trihydroxybenzoate* (5) (5·5 g, 93%), which crystallized from ethyl acetate/light petroleum as colourless prisms, m.p. 125–126° (Found: C, 57·2; H, 3·6. $C_{14}H_{11}ClO_5$ requires C, 57·1; H, 3·8%). ^1H n.m.r. ($CDCl_3$) δ 5·48, s, OCH_2; 6·19, s, ArH; 7·42, 5H, m, Ph; 9·67, 10·34, 10·49, 3s, OH. Mass spectrum *m/z* 296 (0·4%) 294 (M, 1·2), 91 (100).

Benzyl 4-(4′-Benzyloxy-3′-chloro-6′-hydroxy-2′-methylbenzoyloxy)-2,6-dihydroxybenzoate (6)

A mixture of 4-benzyloxy-3-chloro-6-hydroxy-2-methylbenzoic acid (3) (1·45 g, 5 mmol) and benzyl 2,4,6-trihydroxybenzoate (4) (1·30 g, 5 mmol) was dried by azeotropic distillation with toluene. The mixture was then dissolved in toluene (25 ml) and trifluoroacetic anhydride (5 ml), and stirred at room temperature for 24 h. The solvent was evaporated and the residue crystallized from ethyl acetate to give the *depside* (6) (1·2 g, 44%) as colourless crystals, m.p. 143–144° (Found: C, 65·5; H, 4·4; Cl, 6·9. $C_{29}H_{23}ClO_8$ requires C, 65·1; H, 4·3; Cl, 6·6%). ^1H n.m.r. ($CDCl_3$) δ 2·73, s, ArMe; 5·18, s, $ArOCH_2$; 5·51, s, CO_2CH_2; 6·35, s, H3,5; 6·50, s, H5′; 7·40, m, Ph; 9·90, s, 2,6-$(OH)_2$; 11·08, s, 6′-OH. Mass spectrum *m/z* 260 (2·7%), 231 (2·2), 153 (1·2), 149 (2·1), 91 (100).

Benzyl 4-(4′-Benzyloxy-3′-chloro-6′-hydroxy-2′-methylbenzoyloxy)-3-chloro-2,6-dihydroxybenzoate (7)

A mixture of 4-benzyloxy-3-chloro-6-hydroxy-2-methylbenzoic acid (3) (1·45 g, 5 mmol) and benzyl 3-chloro-2,4,6-trihydroxybenzoate (5) (1·38 g, 5 mmol) was dried by azeotropic distillation with toluene. The mixture was then dissolved in toluene (25 ml) and trifluoroacetic anhydride (5 ml), and stirred at room temperature for 24 h. The solvent was evaporated and the residue crystallized from ethyl acetate to give *benzyl 4-(4′-benzyloxy-3′-chloro-6′-hydroxy-2′-methylbenzoyloxy)-3-chloro-2,6-dihydroxybenzoate* (7) (1·2 g, 42%) as colourless crystals, m.p. 156–157° (Found: C, 60·1; H, 4·3; Cl, 7·7. $C_{29}H_{22}Cl_2O_8$ requires C, 60·2; H, 4·2; Cl, 7·7%). ^1H n.m.r. ($CDCl_3$) δ 2·72, s, ArMe; 4·92, s, $ArOCH_2$; 5·51, s, CO_2CH_2; 6·36, 6·45, 2s, ArH; 7·42, m, Ph; 9·87, s, 2,6-$(OH)_2$; 11·05, s, 6′-OH. Mass spectrum *m/z* 391 (2·8%), 351 (5·9), 261 (100).

4-Benzyloxy-2-(4′-benzyloxycarbonyl-3′,5′-dihydroxyphenoxy)-5-chloro-6-methylbenzoic Acid (8)

A solution of benzyl 4-(4′-benzyloxy-3′-chloro-6′-hydroxy-2′-methylbenzoyloxy)-2,6-dihydroxybenzoate (6) (1·1 g, 2·06 mmol) and anhydrous potassium carbonate (0·45 g, 3·3 mmol) in anhydrous dimethyl sulfoxide (22 ml) was stirred at room temperature for 2 h. The reaction mixture was then acidified with cold, dilute hydrochloric acid, extracted with ethyl acetate, and the ethyl acetate extract washed with water and brine, and dried ($MgSO_4$). Evaporation of the solvent gave the crude product 4-benzyloxy-2-(4′-benzyloxycarbonyl-3′,5′-dihydroxyphenoxy)-5-chloro-6-methylbenzoic acid (8) as a brown gum (0·9 g, 80%). ^1H n.m.r. ($CDCl_3$) δ 2·48, s, ArMe; 5·06, s, $ArOCH_2$; 5·46, s, CO_2CH_2; 5·99, s, H2′,6′; 6·54, s, H3; 7·42, m, Ph. Mass spectrum *m/z* 165 (3·3%), 150 (2·6), 137 (1·5), 123 (2·1), 108 (63·7), 91 (46·3), 42 (100).

4-Benzyloxy-2-(4′-benzyloxycarbonyl-2′-chloro-3′,5′-dihydroxphenoxy)-5-chloro-6-methylbenzoic Acid (9)

A solution of benzyl 4-(4′-benzyloxy-3′-chloro-6′-hydroxy-2′-methylbenzoyloxy)-3-chloro-2,6- dihydroxybenzoate (7) (0·61 g, 1·07 mmol) and anhydrous potassium carbonate (0·23 g 1·7 mmol) in anhydrous dimethyl sulfoxide (11 ml) was stirred at room temperature for 2 h. The reaction mixture was then acidified with cold, dilute hydrochloric acid, extracted with ethyl acetate, and the ethyl acetate extract washed with water and brine, and dried ($MgSO_4$). Evaporation of the solvent gave the crude product (9) (0·59 g, 96%) as a brown microcrystalline solid. ^{1}H n.m.r. ($CDCl_3$) δ 2·50, s, ArMe; 5·07, s, $ArOCH_2$; 5·49, s, CO_2CH_2; 5·85, 6·50, 2s, ArH; 7·35, 7·42, 2m, Ph; 9·75, 10·39, 2s, OH.

Benzyl 6-Benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9-oxo-9H-xanthen-2-carboxylate (10)

The carboxylic acid (8) (0·9 g, 1·7 mmol) was dried by azeotropic distillation with toluene and then dissolved in anhydrous toluene (21 ml) and stirred at 0°. Trifluoroacetic anhydride (4·1 ml) was then added and the mixture was stirred first at 0° for 10 min, then at room temperature for 22 h. The solvent was evaporated and the residue crystallized from ethyl acetate/cyclohexane to give *benzyl 6-benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9-oxo-9H-xanthen-2-carboxylate* (10) (0·52 g, 59%) as a colourless microcrystalline solid, m.p. 241–242° (Found: C, 67·5; H, 4·2; Cl, 7·0. $C_{29}H_{21}ClO_7$ requires C, 67·4; H, 4·1; Cl, 6·9%). ^{1}H n.m.r. ($CDCl_3$) δ 3·01, s, ArMe; 5·26, 2H, s, $ArOCH_2$; 5·48, s, CO_2CH_2; 6·27, s, H4; 6·81, s, H5; 7·42, m, Ph; 12·55, 13·12, 2s, OH. Mass spectrum *m/z* 518 (0·2%), 516 (M, 0·7), 91 (100).

Benzyl 6-Benzyloxy-4,7-dichloro-1,3-dihydroxy-8-methyl-9-oxo-9H-xanthen-2-carboxylate (11)

The carboxylic acid (9) (0·59 g, 1·04 mmol) was dried by azeotropic distillation with toluene and then dissolved in anhydrous toluene (21 ml) and stirred at 0°. Trifluoroacetic anhydride (3·6 ml) was then added and the mixture was stirred first at 0° for 10 min, then at room temperature for 22 h. The solvent was removed and the product crystallized from ethyl acetate/cyclohexane to give *benzyl 6-benzyloxy-4,7-dichloro-1,3-dihydroxy-8-methyl-9-oxo-9H-xanthen-2-carboxylate* (11) (0·5 g, 87%) as pale yellow microcrystals, m.p. 256–257° (Found: C, 63·6; H, 3·6; Cl, 12·4. $C_{29}H_{20}Cl_2O_7$ requires C, 63·2; H, 3·7; Cl, 12·9%). ^{1}H n.m.r. ($CDCl_3$) δ 3·02, s, ArMe; 5·29, s, $ArOCH_2$; 5·50, s, CO_2CH_2; 6·99, s, ArH; 7·43, m, Ph. Mass spectrum *m/z* 552 (0·15%), 550 (M, 0·2), 91, (100).

6-Benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9H-xanthen-9-one (12)

A mixture of the benzyl ester (10) (0·3 g, 0·58 mmol), dimethyl sulfoxide (4·2 ml), potassium hydroxide (0·5 g) and water (1 ml) was stirred and heated in a nitrogen atmosphere at 100–110° for 5 h, and was then diluted with water. The basic aqueous layer was poured into cold, dilute hydrochloric acid, extracted with ethyl acetate, and the organic extract washed with water and saturated brine, and dried ($MgSO_4$). After removal of the solvent, the residue was purified by radial chromatography (SiO_2) by using 2–40% ethyl acetate/light petroleum as eluent. The major band afforded *6-benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9H-xanthen-9-one* (12) (0·1 g, 45%) as pale brown plates, m.p. 290–292° (Found: C, 66·0; H, 4·0. $C_{21}H_{15}ClO_5$ requires C, 65·9; H, 3·9%). ^{1}H n.m.r. ($CDCl_3$) δ 3·02, s, ArMe; 5·24, s, OCH_2; 6·27, s, H2,4; 6·81, s, H5; 7·42, m, Ph. Mass spectrum *m/z* 384 (9%), 382 (M, 36), 91 (100).

7-Chloro-1,3,6-trihydroxy-8-methyl-9-oxo-9H-xanthen-2-carboxylic Acid (13)

A solution of benzyl 6-benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9-oxo-9*H*-xanthen-2-carboxylate (11) (0·1 g, 0·19 mmol) in anhydrous dichloromethane (16 ml) was treated with a solution of boron trichloride in dichloromethane (1 M, 1·8 ml), and the mixture was stirred at room temperature for 3 h. The mixture was then poured into ice-water,

concentrated to remove the dichloromethane solvent, filtered, and the precipitate washed with water. The yellow precipitate crystallized from dimethylformamide to give *7-chloro-1,3,6-trihydroxy-8-methyl-9-oxo-9*H*-xanthen-2-carboxylic acid* (13) (0·06 g, 93%) as yellow needles, which decomposed at 360° (Found: C, 53·3; H, 2·7. $C_{15}H_9ClO_7$ requires C, 53·5; H, 2·7%). ^{1}H n.m.r. [$(CD_3)_2SO$] δ 2·86, s, ArMe; 6·32, s, H4; 6·88, s, H5. Mass spectrum *m/z* 338 (0·4%), 336 (M, 1·4), 292 (100).

*7-Chloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (14)*

(i) A solution of 6-benzyloxy-7-chloro-1,3-dihydroxy-8-methyl-9*H*-xanthen-9-one (12) (0·1 g, 0·26 mmol) in anhydrous dichloromethane (30 ml) was treated with a solution of boron trichloride in dichloromethane (1 M, 2 ml) and the mixture was stirred at room temperature for 2 h. The mixture was then poured into ice-water, extracted with chloroform, and the organic layer washed with saturated sodium hydrogen carbonate solution, water and saturated brine, and dried ($MgSO_4$). After removal of the solvent the residue was purified by radial chromatography over silica gel with ethyl acetate/light petroleum as eluent. The major band yielded 7-chloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (14) (0·062 g, 81%) as pale yellow-brown crystals, m.p. 284–285° (lit.[10] 285–286°), identical with authentic material (t.l.c., h.p.l.c, ^{1}H n.m.r.).

(ii) A mixture of 7-chloro-1,3,6-trihydroxy-8-methyl-9-oxo-9*H*-xanthen-2-carboxylic acid (13) (0·15 g, 0·446 mmol), dimethyl sulfoxide (3 ml), potassium hydroxide (0·38 g) and water (1 ml) was stirred and heated at 100–110° for 5 h, and then diluted with water. The basic aqueous layer was acidified by addition to cold, dilute hydrochloric acid, then extracted with ethyl acetate, and the organic extract was washed with water and saturated brine, and dried ($MgSO_4$). After removal of the solvent, the residue was crystallized from ethyl acetate/cyclohexane to yield 7-chloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (14) (0·1 g, 76%), identical with the above material.

*Chlorination of 7-Chloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (14)*

A solution of 7-chloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (14) (0·1 g, 0·34 mmol), *N*-chlorosuccinimide (0·051 g) and several crystals of toluene-4-sulfonic acid in dioxan (12 ml) was heated under reflux for 20 h. The solution was then poured into water and extracted with ethyl acetate. The organic extract was washed with water and brine, and dried ($MgSO_4$). The crude product obtained on evaporation of the solvent was purified by radial chromatography (SiO_2) with 40% ethyl acetate/light petroleum as eluent. The faster moving band yielded 4,7-dichloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (15) (0·03 g, 27%) which crystallized from the eluent as yellow crystals, m.p. 297–298° (lit.[7] 290–293°) (Found: mol. wt, 325·9748. Calc. for $^{12}C_{14}{}^1H_8{}^{35}Cl_2{}^{16}O_5$: 325·9749). ^{1}H n.m.r.[7] [$(CD_3)_2CO$] δ 2·93, s, ArMe; 6·35, s, H2; 6·97, s, H5; 9·64, s, OH. Mass spectrum *m/z* 328 (0·8%), 326 (M, 1·0), 292 (0·7), 43 (100).

The slower moving band contained the isomer 2,7-dichloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (16) (0·012 g, 11%), which crystallized from the eluent as yellow crystals, m.p. 296–298° (lit.[7] 298–299°) (Found: mol. wt, 325·9748. Calc. for $^{12}C_{14}{}^1H_8{}^{35}Cl_2{}^{16}O_5$: 325·9749). ^{1}H n.m.r.[2] [$(CD_3)_2CO$] δ 2·95, s, ArMe; 6·50, s, H4; 6·91, s, H5; 8·85, s, OH. Mass spectrum *m/z* 328 (23%), 326 (M, 31), 292 (69), 43 (100).

*4,7-Dichloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (15)*

A mixture of the benzyl ester (11) (0·36 g, 0·653 mmol), dimethyl sulfoxide (4·7 ml), potassium hydroxide (0·56 g) and water (1 ml) was stirred in a nitrogen atmosphere, heated under reflux for 45 min and then diluted with water. The basic aqueous layer was poured into cold, dilute hydrochloric acid, extracted with ethyl acetate, and the organic extract washed with water and saturated brine, and dried ($MgSO_4$). After removal of the solvent, the residue was purified by radial chromatography with 5–70% ethyl acetate/light petroleum. The major band afforded 4,7-dichloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (15) (0·20 g, 94%) as yellow crystals, m.p. 297–298°, identical with the material prepared above.

6-Benzyloxy-4,7-dichloro-1,3-dihydroxy-8-methyl-9H-xanthen-9-one (17)

A mixture of benzyl 6-benzyloxy-4,7-dichloro-1,3-dihydroxy-8-methyl-9-oxo-9*H*-xanthen-2-carboxylate (11) (0·4 g, 0·73 mmol), dimethyl sulfoxide (6 ml), potassium hydroxide (0·6 g) and water (4 ml) was stirred and heated in a nitrogen atmosphere at 120–135° for 1·5 h. The cooled solution was then poured into cold, dilute hydrochloric acid, and the solid filtered off. The solid product was crystallized from dimethylformamide to give *6-benzyloxy-4,7-dichloro-1,3-dihydroxy-8-methyl-9H-xanthen-9-one* (17) (0·28 g, 92%) as yellow crystals, m.p. 272–274° (Found: mol. wt, 416·0218. $^{12}C_{21}{}^{1}H_{14}{}^{35}Cl_2{}^{16}O_5$ requires mol. wt, 416·0218). The homogeneity of this compound was confirmed by ^{1}H n.m.r. spectroscopy, h.p.l.c., and t.l.c. in three independent solvent systems. ^{1}H n.m.r. [$(CD_3)_2CO$)] δ 2·92, s, ArMe; 5·45, s, OCH_2; 6·43, s, H2; 7·26, s, H5; 7·47, m, Ph. Mass spectrum *m/z* 418 (1·4%), 416 (M, 1·8), 91 (100).

6-Benzyloxy-4,7-dichloro-1-hydroxy-3-methoxy-8-methyl-9H-xanthen-9-one (18)

A mixture of 6-benzyloxy-4,7-dichloro-1,3-dihydroxy-8-methyl-9*H*-xanthen-9-one (17) (0·48 g, 1·15 mmol), dimethyl sulfate (0·45 g, 3·6 mmol), potassium carbonate (0·9 g), acetone (25 ml) and dimethylformamide (10 ml) was stirred and refluxed for 20 h. The cooled reaction mixture was then poured into cold, dilute hydrochloric acid and the precipitated product was filtered off. The product was crystallized from dimethylformamide to give *6-benzyloxy-4,7-dichloro-1-hydroxy-3-methoxy-8-methyl-9H-xanthen-9-one* (18) (0·35 g, 71%) as pale yellow crystals, m.p. 258–259° (Found: C, 61·4; H, 3·6; Cl, 16·7. $C_{22}H_{16}Cl_2O_5$ requires C, 61·3; H, 3·7; Cl, 16·4%). ^{1}H n.m.r. [$(CD_3)_2CO$)] δ 2·92, s, ArMe; 4·04, s, OMe; 5·49, s, OCH_2; 6·62, s, H2; 7·25, s, H5; 7·45, m, Ph. Mass spectrum *m/z* 432 (2·2%), 430 (M, 3·0), 91 (100).

4,7-Dichloro-1,6-dihydroxy-3-methoxy-8-methyl-9H-xanthen-9-one (19)

A solution of 6-benzyloxy-4,7-dichloro-1-hydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (18) (0·1 g, 0·23 mmol) in anhydrous dichloromethane (20 ml) was stirred at −10° while boron trichloride (1·4 mmol) in dichloromethane (1·4 ml) was added slowly. The mixture was stirred at −10° for 1 h and at room temperature for a further 4 h, and then poured into ice-water. The dichloromethane solvent was evaporated under reduced pressure and the precipitate filtered off and washed with water. The crude product was crystallized from ethyl acetate/cyclohexane to give 4,7-dichloro-1,6-dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (19) (70 mg, 89%) as yellow needles, m.p. 233–236° (dec.) (lit.[7] 246–247°) (Found: C, 52·7; H, 2·9; Cl, 20·4. Calc. for $C_{15}H_{10}Cl_2O_5$: C, 52·8; H, 3·0; Cl, 20·8%). ^{1}H n.m.r. ($CDCl_3$) δ 3·01, s, ArMe; 3·97, s, OMe; 6·40, s, H2; 7·05, s, H5; 8·15, 13·30, 2s, OH. Mass spectrum *m/z* 344 (11%), 342 (64), 340 (M, 100), 311 (9), 306 (3).

Chlorination of 4,7-Dichloro-1,6-dihydroxy-3-methoxy-8-methyl-9H-xanthen-9-one (19)

A solution of 4,7-dichloro-1,6-dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (19) (0·102 g, 0·3 mmol), *N*-chlorosuccinimide (0·06 g, 0·45 mmol) and several crystals of toluene-4-sulfonic acid in dimethylformamide (10 ml) was heated and stirred at 100° for 20 h. The solution was then cooled, poured into water and extracted with ethyl acetate. The organic extract was washed with water and brine, and dried ($MgSO_4$). The crude product obtained on evaporation of the solvent was purified by preparative thin-layer chromatography (SiO_2) by using 50% ethyl acetate/light petroleum as eluent. Two main bands developed. The faster moving band yielded *2,4,7-trichloro-1,6-dihydroxy-3-methoxy-8-methyl-9H-xanthen-9-one* (20) (20 mg, 18%) which crystallized from the eluent as yellow crystals, m.p. 257–259° (dec.) (Found: mol. wt, 373·9515. $^{12}C_{15}{}^{1}H_9{}^{35}Cl_3{}^{16}O_5$ requires mol. wt, 373·9516). The homogeneity of this compound was confirmed by ^{1}H n.m.r. spectroscopy, h.p.l.c., and t.l.c. in three independent solvent systems. ^{1}H n.m.r. [$(CD_3)_2CO$] δ 2·95, s, Me; 4·02, s, OMe; 7·05, s, H5; 7·44, 13·93, 2s, OH. Mass spectrum *m/z* 380 (4%), 378 (32), 376 (97), 374 (M, 100), 340 (44).

The slower moving band contained the isomer 4,5,7-trichloro-1,6-dihydroxy-3-methoxy-8-methyl-9*H*-xanthen-9-one (21) (10 mg, 9%), which crystallized from the eluent as yellow crystals, m.p. 285–287° (dec.) alone or admixed with authentic material (lit.[9] 294–295°) (Found: mol. wt, 373·9515. Calc. for $^{12}C_{15}{}^{1}H_{9}{}^{35}Cl_{3}{}^{16}O_{5}$: 373·9516). ^{1}H n.m.r. [$(CD_3)_2CO$] δ 2·93, s, Me; 4·02, s, OMe; 6·50, s, H4. Mass spectrum[9] *m/z* 380 (4%), 378 (32), 376 (97), 374 (M, 100), 344 (5), 339 (3), 310 (10).

*2,4,7-Trichloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (22)*

A solution of sulfuryl chloride (0·06 mmol) in anhydrous dioxan (1 ml) was added dropwise to a solution of 4,7-dichloro-8-methyl-1,3,6-trihydroxy-9*H*-xanthen-9-one (15) (0·02 g, 0·06 mmol) in anhydrous dioxan (1 ml), and the mixture stirred at room temperature for 4·5 h. Evaporation of the solvent under reduced pressure then gave the crude product. This was purified by radial chromatography (silica gel) by using 30–100% ethyl acetate/light petroleum eluent to give *2,4,7-trichloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one* (22) (0·013 g, 60%), m.p. 228–229° (Found: mol. wt, 359·9359. $^{12}C_{14}{}^{1}H_{7}{}^{35}Cl_{3}{}^{16}O_{5}$ requires mol. wt, 359·9359). The homogeneity of this compound was confirmed by ^{1}H n.m.r. spectroscopy, h.p.l.c., and t.l.c. in three independent solvent systems. ^{1}H n.m.r. [$(CD_3)_2CO$)] δ 2·92, s, ArMe; 6·96, s, H5; 8·92, s, OH. Mass spectrum *m/z* 366 (4%), 364 (31), 362 (94), 360 (100, M), 328 (8), 327 (6), 326 (13), 325 (7), 297 (4). Standard t.l.c.[18,19] R_F values: $R_{F(A)}$ 0·51; $R_{F(B)}$ 0·50; $R_{F(C)}$ 0·34; $R_{F(E)}$ 0·04. Standard h.p.l.c.[20] R_t value: 6·90 min.

3,5-Dichloro-2-hydroxy-4-methoxy-6-methylbenzoic Acid (23)

A mixture of ethyl 3,5-dichloro-2-hydroxy-4-methoxy-6-methylbenzoate[21] (4·7 g, 16·8 mmol), dimethyl sulfoxide (100 ml), potassium hydroxide (3·7 g) and water (17 ml) was stirred and heated at 90–100° for 4 h. The mixture was then cooled, diluted with water and extracted with either to remove any unchanged starting material. The basic aqueous layer was poured into cold, dilute hydrochloric acid, extracted with ether and the ethereal extract washed with water, with saturated brine, and dried ($MgSO_4$). After removal of solvent the residue was crystallized from cyclohexane to give *3,5-dichloro-2-hydroxy-4-methoxy-6-methybenzoic acid* (23) (3·3 g, 78%) as colourless crystals, m.p. 199–200° (Found: C, 43·0; H, 3·4; Cl, 28·5. $C_9H_8Cl_2O_4$ requires C, 43·1; H, 3·2; Cl, 28·2%). ^{1}H n.m.r. ($CDCl_3$) δ 2·60, s, ArMe; 3·85, s, OMe. Mass spectrum *m/z* 252 (7·9%), 250 (M, 10·8), 231 (100).

Benzyl 3-Chloro-4-(3′,5′-dichloro-2′-hydroxy-4′-methoxy-6′-methylbenzoyloxy)-2,6-dihydroxybenzoate (24)

A solution of 3,5-dichloro-2-hydroxy-4-methoxy-6-methylbenzoic acid (23) (502 mg, 2 mmol) and benzyl 3-chloro-2,4,6-trihydroxybenzoate (5) (589 mg, 2 mmol) in anhydrous toluene (10 ml), and trifluoroacetic anhydride (2·5 ml) was stirred for 20 h at room temperature. After removal of the solvent, the product was dissolved in dichloromethane and purified by radial chromatography (SiO_2) by using 2·5–20% ethyl acetate/light petroleum as eluent. The first band was rechromatographed with 5–10% ethyl acetate/light petroleum as eluent to give pure *benzyl 3-chloro-4-(3′,5′-dichloro-2′-hydroxy-4′-methoxy-6′-methylbenzoyloxy)-2,6-dihydroxybenzoate* (24) (350 mg, 33%) as colourless prisms, m.p. 117° (Found: C, 52·3; H, 3·5; Cl, 20·2. $C_{23}H_{17}Cl_3O_8$ requires C, 52·4; H, 3·3; Cl, 20·2%). ^{1}H n.m.r. ($CDCl_3$) δ 2·77, s, ArMe; 3·97, s, OMe; 5·54, s, OCH_2; 6·45, s, ArH; 7·44, s, Ph; 9·80, 10·50, 10·74, 3s, OH. Mass spectrum *m/z* 294 (1·5%), 91 (100).

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Benzyl 4,5,7-Trichloro-1,3-dihydroxy-6-methoxy-8-methyl-9-oxo-9H-xanthen-2-carboxylate (26)

A mixture of benzyl 3-chloro-4-(3′,5′-dichloro-2′-hydroxy-4′-methoxy-6′-methylbenzoyloxy)-2,6-dihydroxybenzoate (24) (0·264 g, 0·5 mmol) and freshly dried potassium carbonate (69 mg) was stirred in anhydrous dimethyl sulfoxide (5 ml) at room temperature for 19 h. The reaction mixture was then poured into cold, dilute hydrochloric acid, extracted with ethyl acetate, and the organic extract washed with water and brine, and dried ($MgSO_4$). After filtration and removal of the solvent, the product was washed with light petroleum to give crude 2-(4′-benzyloxycarbonyl-2′-chloro-3′,5′-dihydroxyphenoxy)-3,5-dichloro-4-methoxy-6-methylbenzoic acid (25) (270 mg). A solution of this acid in anhydrous toluene (6 ml) was cooled to 0° and stirred with trifluoroacetic anhydride (2 ml) for 15 min and then at room temperature for 21 h. After removal of the solvent, the residue was warmed in ethyl acetate, cooled and filtered off to yield *benzyl 4,5,7-trichloro-1,3-dihydroxy-6-methoxy-8-methyl-9-oxo-9H-xanthen-2-carboxylate* (26) (58 mg, 23%) which crystallized from ethyl acetate/cyclohexane as yellow crystals, m.p. 235° (Found: C, 54·3; H, 2·7; Cl, 20·7. $C_{23}H_{15}Cl_3O_7$ requires C, 54·2; H, 3·0; Cl, 20·9%). ^1H n.m.r. ($CDCl_3$) δ 2·98, s, ArMe; 4·03, s, OMe; 5·50, s, OCH_2; 7·45, m, Ph; 13·27, 13·32, 2s, OH. Mass spectrum *m/z* 512 (0·2%), 510 (0·5), 508 (M, 0·5), 91 (100).

4,5,7-Trichloro-1,3-dihydroxy-6-methoxy-8-methyl-9H-xanthen-9-one (28) and 4,5,7-Trichloro-1,3,6-trihydroxy-8-methyl-9H-xanthen-9-one (29)

A solution of boron trichloride in dichloromethane (11 ml, 0·1 M) was added dropwise to a solution of benzyl 4,5,7-trichloro-1,3-dihydroxy-6-methoxy-8-methyl-9-oxo-9*H*-xanthen-2-carboxylate (24) (51 mg, 0·1 mmol) in anhydrous dichloromethane (40 ml) at −10°. The solution was stirred for a further 1 h at this temperature and then at room temperature for 4 h. The solution was poured into cold water, extracted with ethyl acetate, the organic extract washed with water and brine, and dried ($MgSO_4$). Evaporation of the solvent gave the crude acid 4,5,7-trichloro-1,3-dihydroxy-6-methoxy-8-methyl-9-oxo-9*H*-xanthen-2-carboxylic acid (27) (26 mg). A solution of this acid, dimethyl sulfoxide (3 ml), potassium hydroxide (100 mg) and water (1 ml) was stirred at 90–95° for 4·5 h. After cooling, the mixture was poured into cold, dilute hydrochloric acid, extracted with ethyl acetate, the organic extract washed with water and brine, and dried ($MgSO_4$). The residue obtained on removal of the solvent was separated by radial chromatography by using 10–20% ethyl acetate/light petroleum as eluent. The faster moving band yielded *4,5,7-trichloro-1,3-dihydroxy-6-methoxy-8-methyl-9H-xanthen-9-one* (28) (4·6 mg, 12%) which crystallized from acetone in yellow needles, m.p. 298–300° (dec.) (Found: mol. wt, 373·9518. $C_{15}H_9Cl_3O_5$ requires mol. wt, 373·9515). The homogeneity of this compound was confirmed by ^1H n.m.r. spectroscopy, h.p.l.c., and t.l.c. in three independent solvent systems. ^1H n.m.r. ($CDCl_3$) 2·99, s, ArMe; 4·05, s, OMe; 6·51, s, ArH, 12·84, s, OH. Mass spectrum *m/z* 380 (4%), 379 (6), 378 (30), 377 (18), 376 (93), 375 (18), 374 (M, 100), 342 (21), 341 (7), 340 (27), 335 (6), 333 (20), 331 (19), 299 (5), 297 (8), 189 (9), 188 (11), 187 (13), 170 (5), 163 (7), 162 (9), 145 (7), 135 (6), 134 (5), 126 (5), 125 (6), 123 (5), 113 (8), 111 (14), 110 (6), 109 (14), 108 (5), 103 (5), 101 (5).

The second band yielded 4,5,7-trichloro-1,3,6-trihydroxy-8-methyl-9*H*-xanthen-9-one (29) (6·9 mg, 19%) which crystallized from aqueous acetone as yellow needles, m.p. 308–309° (dec.) [lit.[9] 307–308° (dec.)] (Found: mol. wt, 359·9359. Calc. for $^{12}C_{14}{}^1H_7{}^{35}Cl_3{}^{16}O_5$: 359·9359). ^1H n.m.r.[9] [$(CD_3)_2CO$)] δ 2·95, s, ArMe; 6·46, s, H2; 13·41, s, OH. Mass spectrum *m/z* 366 (4%), 364 (33), 362 (99), 360 (100, M), 359 (5), 331 (5), 325 (10), 297 (6). Standard t.l.c.[18,19] R_F values: $R_{F(A)}$ 0·47; $R_{F(B)}$ 0·55; $R_{F(C)}$ 0·37; $R_{F(E)}$ 0·07. Standard h.p.l.c.[20] R_t value: 6·95 min.

Lichens Examined

(i) Lecanora flavo-pallescens *Nyl.*—The lichen was collected on bark, New Zealand (locality not specified), C. Knight (UPS).

(ii) Lecanora sulphurata *(Ach.) Nyl.*—The lichen was collected on rocks, Cepelarska planina: in valle rivuli 'Kriva r.' pr. Pasmakli, Bulgaria, Dr O. Szatala, Lichenes Bulgariae (UPS); on

schistose rocks, var insula Port Cros, Les Crétes du Sud, France, Y. Rondon in A. Vézda, Lichenes Selecti Exsiccati, No. 1631 (BM).

(iii) Micarea austroternaria *var.* isabellina *Coppins & Kantvilas ined.*—The lichen was collected on peat in buttongrass moorland, foothills of Arthur Range, above Port Davey Track, 600 m, G. Kantvilas 505/84 (ANUC).

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