Regioselective Carboxylation of 9-Xanthenones with Manganese(III) Acetate

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Seven 9-xanthenones were oxidized with manganese(III) acetate to give carboxy-, dicarboxy-, (acetoxymethyl)-(carboxy)-, (carboxy)(hydroxymethyl)-, and acetoxymethyl-9-xanthenones, and to yield small amounts of (carboxymethyl)(carboxy)-, carboxymethyl-, (acetoxymethyl)(carboxymethyl)-, bis(acetoxymethyl)-, and diacetoxymethyl-9-xanthenones. The carboxyl group was preferentially introduced into the peri positions and the acetoxymethyl groups were located at positions ortho to the methoxyl or methyl group. The regioselectivity and mechanism of the carboxylation reaction is discussed briefly.

We have previously reported that the oxidation of 2-hydroxybenzophenones with manganese(III) acetate gave the corresponding 9-xanthenones and trace amounts of acetoxymethylated 9-xanthenones as by-products.[1] The acetoxymethylated products were considered to be formed by further oxidation of 9-xanthenones. This prompted us to study the reaction of 9-xanthenones with manganese(III) acetate.

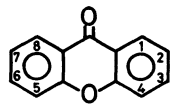
The reaction of several aromatic compounds with manganese(III) acetate was first investigated by S. A. Zonis.[2] This oxidation reaction mainly yielded acetoxylated compounds and ketones, and was kinetically studied by Dewar *et al.*[3] However, on oxidation under vigorous reaction conditions acetoxymethylation occurred.[4,5] This reaction specifically takes place in the manganese(III) acetate oxidation and to some extent in lead(IV) acetate oxidation.[6] Heiba and his coworkers oxidized toluene with manganese(III) acetate and obtained acetoxymethyl derivatives.[4] They studied the reaction mechanism kinetically and concluded that a carboxymethyl radical, $\cdot CH_2COOH$, formed directly from manganese(III) acetate, is involved in this reaction. We carried out the oxidation of 9-xanthenones, and obtained carboxy and acetoxymethyl derivatives. In this paper we will discuss the regioselectivity and the mechanisms of these carboxylation reactions of substituted 9-xanthenones.

Results and Discussion

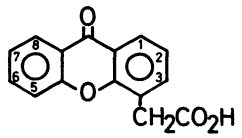
The compounds studied were 9-xanthenone (**1a**), 3-methoxy-9-xanthenone (**1b**), 3,6-dimethoxy-9-xanthenone (**1c**), 2,3,6-trimethoxy-9-xanthenone (**1d**), 3-methoxy-4-methyl-9-xanthenone (**1e**), 3-methoxy-5-methyl-9-xanthenone (**1f**), and 1-methoxy-3-methyl-9-xanthenone (**1g**).

9-Xanthenones were oxidized with manganese(III) acetate dihydrate in boiling acetic acid containing acetic anhydride and the products were separated by TLC. The results are shown in Table 1 and Fig. 1.

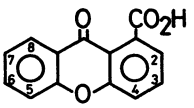
When 9-xanthenone (**1a**) was oxidized with manganese(III) acetate, it was found that a significant amount



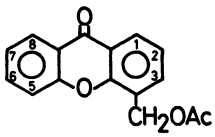
1a
1b: 3-CH_3O
1c: 3,6-$(CH_3O)_2$
1d: 2,3,6-$(CH_3O)_3$
1e: 3-CH_3O-4-CH_3
1f: 3-CH_3O-5-CH_3
1g: 1-CH_3O-3-CH_3
12b: 2-HO_2CCH_2-3-CH_3O
16g: 1-CH_3O-3-$AcOCH_2$
19a: 1-$(AcO)_2CH$



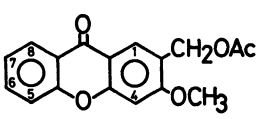
11b: 3-CH_3O
11c: 3,6-$(CH_3O)_2$
11d: 2,3,6-$(CH_3O)_3$
11g: 6-CH_3-8-CH_3O
13g: 5-$AcOCH_2$-6-CH_3-8-CH_3O



2a
2b: 6-CH_3O
2c: 3,6-$(CH_3O)_2$
2d: 2,3,6-$(CH_3O)_3$
2e: 5-CH_3-6-CH_3O
2f: 4-CH_3-6-CH_3O
2g: 6-CH_3-8-CH_3O
3d: 3,6,7-$(CH_3O)_3$
3e: 3-CH_3O-4-CH_3
4a: 8-HO_2C
4e: 3-CH_3O-4-CH_3-8-HO_2C
5e: 3-CH_3O-4-CH_3-5-HO_2CCH_2
6b: 5-$AcOCH_2$-6-CH_3O
6f: 4-CH_3-5-$AcOCH_2$-6-CH_3O
6g: 5-$AcOCH_2$-6-CH_3-8-CH_3O
7a: 4-$AcOCH_2$
7b: 3-CH_3O-4-$AcOCH_2$
7c: 3,6-$(CH_3O)_2$-4-$AcOCH_2$
7d: 3,6,7-$(CH_3O)_3$-4-$AcOCH_2$
8c: 3,6-$(CH_3O)_2$-4,5-$(AcOCH_2)_2$
9a: 4-$HOCH_2$
9b: 3-CH_3O-4-$HOCH_2$
9c: 3,6-$(CH_3O)_2$-4-$HOCH_2$
9d: 3,6,7-$(CH_3O)_3$-4-$HOCH_2$
10b: 5-$HOCH_2$-6-CH_3O



14a
14b: 3-CH_3O
14c: 3,6-$(CH_3O)_2$
14d: 3,6,7-$(CH_3O)_3$
14f: 3-CH_3O-5-CH_3
14g: 1-CH_3O-3-CH_3
17c: 3,6-$(CH_3O)_2$-5-$AcOCH_2$
17g: 1-CH_3O-3-CH_3-5-$AcOCH_2$
18c: 3,6-$(CH_3O)_2$-7-$AcOCH_2$



15b
15c: 6-CH_3O
15d: 6,7-$(CH_3O)_2$
15f: 5-CH_3

Fig. 1. 9-Xanthenones (**1a—g**) and the oxidation products **2—19**.

Table 1. Oxidation of 9-xanthenones (**1a—g**) with manganese(III) acetate in acetic acid containing acetic anhydride at reflux temperature

Entry	Substrate	Reaction conditions: Molar ratio of substrate: oxidant	Reaction conditions: Time / min	Recovered substrate (%)	Product (yield/%)[a,b]
1	**1a**	1 : 10	40	20	**2a**(30), **4a**(12), **9a**(6), **14a**(2), **19a**(1)
2	**1b**	1 : 12	43	13	**2b**(11), **9b**(4), **10b**(3), **14b**(10), **15b**(4)
3[c]	**1b**	1 : 12	24	26	**2b**(10), **9b**(4), **10b** (4), **11b** (10), **12b**(3), **14b**(6), **15b**(3)
4	**1c**	1 : 12	29	10	**2c**(7), **9c**(14), **11c**(4), **14c**(13), **15c**(6), **17c**(4), **18c**(3)
5[d]	**1c**	1 : 12	50	11	**2c**(5), **7c**(5), **8c**(5), **9c**(6), **11c**(3), **14c**(16), **15c**(7), **17c**(7), **18c**(3)
6	**1d**	1 : 10	27	23	**2d**(7), **3d**(3), **9d**(5), **11d**(3), **14d**(16), **15d**(5)
7	**1e**	1 : 10	30	17	**2e**(11), **3e**(28), **4e**(11), **5e**(4), **9b**(7), **14b**(3)
8	**1f**	1 : 10	26	15	**2f**(20), **6f**(7), **14f**(8), **15f**(3)
9	**1g**	1 : 10	30	12	**2g**(10), **6g**(12), **11g**(3), **13g**(5), **14g**(25), **16g**(1), **17g**(4)

a) The yields are based on the amount of the substrate consumed. b) The yields of the acidic products are calculated as their methyl esters. c) Potassium acetate (60 mmol) was added to the reaction mixture. d) This oxidation was carried out under an atmosphere of nitrogen.

of acidic compounds were present in the product mixture, from which five compounds (**2a**, **4a**, **9a**, **14a**, and **19a**) were isolated (Entry 1). The IR spectrum of **2a** indicated absorptions at 1720 and 2500—3200 cm^{-1} due to carboxyl group. Its NMR spectrum showed a broad singlet at $\delta=13.0$ for a carboxylic acid and a multiplet at $\delta=7.4$—8.3 for seven aromatic protons, one of which is deshielded. Therefore, the structure of **2a** was determined to be 1-carboxy-9-xanthenone the melting point of which was close to the literature value.[10] **4a** was identified as 1,8-dicarboxy-9-xanthenone by methylation. The NMR spectrum of the methyl ester of **9a** indicated the presence of a hydroxymethyl group, $-CH_2OH$, $\delta=3.5$ (1H, broad s) and 4.99 (2H, s), and an AB quartet due to two aromatic protons $\delta=7.19$ (1H, d, $J=7.8$ Hz, $H_{(2)}$) and 7.80 (1H, d, $J=7.8$ Hz, $H_{(3)}$). In its IR spectrum two carbonyl and a hydroxyl absorptions appeared at 1645, 1745, and 3300—3500 cm^{-1}, respectively. When the corresponding methyl ester was treated with acetic anhydride in pyridine–acetic acid, the NMR spectrum of the product (**7a**) showed an acetoxymethyl group at $\delta=2.16$ (3H, s) and $\delta=5.46$ (2H, s). Accordingly, these spectral data supported the 1-carboxy-4-hydroxymethyl-9-xanthenone (**9a**) structure. Other acidic products were also formed in this oxidation reaction, but they could not be purified by TLC. **14a** was identified as 4-acetoxymethyl-9-xanthenone by comparison of its NMR spectrum with those of other 4-acetoxymethylated derivatives. The NMR spectrum of **19a** indicated the presence of a diacetoxymethyl group, $-CH(OAc)_2$, $\delta=2.16$ (6H, s) and 8.86 (1H, s), and the disappearance of one of the deshielded aromatic protons in **1a**. The IR spectrum showed carbonyl absorptions at 1686, 1755, and 1768 cm^{-1}. These spectroscopic properties are consistent with the 1-diacetoxymethyl-9-xanthenone (**19a**) structure.

The reaction of 3-methoxy-9-xanthenone (**1b**) with manganese(III) acetate gave 1-carboxy-6-methoxy- (**2b**), 1-carboxy-4-hydroxymethyl-3-methoxy- (**9b**), 1-carboxy-5-hydroxymethyl-6-methoxy- (**10b**), 4-acetoxymethyl-3-methoxy- (**14b**), and 2-acetoxymethyl-3-methoxy-9-xanthenone (**15b**) (Entry 2). The structures were confirmed by examining their IR, mass, and NMR spectra, and by elemental analyses. The NMR spectrum of **14b** showed the methylene proton of the acetoxymethyl group at $\delta=5.47$, while the methylene proton of **15b** appeared at $\delta=5.18$.

3,6-Dimethoxy-9-xanthenone (**1c**) gave 1-carboxy-3,6-dimethoxy- (**2c**), 1-carboxy-4-hydroxymethyl-3,6-dimethoxy- (**9c**), 4-carboxymethyl-3,6-dimethoxy- (**11c**), 4-acetoxymethyl-3,6-dimethoxy- (**14c**), 2-acetoxymethyl-3,6-dimethoxy- (**15c**), 4,5-bis(acetoxymethyl)-3,6-dimethoxy- (**17c**), and 2,5-bis(acetoxymethyl)-3,6-dimethoxy-9-xanthenone (**18c**) (Entry 4). The structure of the methyl ester of **11c** was elucidated from the spectroscopic evidence showing the presence of a methoxycarbonylmethyl group $\delta=3.72$ (3H, s) and 3.90 (2H, s), an AB quartet due to two aromatic protons $\delta=7.02$ (1H, d, $J=10.2$ Hz, $H_{(2)}$) and 8.29 (1H, d, $J=10.2$ Hz, $H_{(1)}$), and *m/e* 328.0939 (M^+). **18c** was not separated from **17c** because both have the same R_f values on TLC. However, the NMR spectrum of the mixture could be explained by assuming that it consists of two compounds, **17c** and **18c**. Elemental analysis also agreed with the calculated values for the molecular formula of $C_{21}H_{20}O_8$ that is the same for both compounds.

2,3,6-Trimethoxy-9-xanthenone (**1d**) yielded **2d**, **3d**, **9d**, **11d**, **14d**, and **15d** (Entry 6).

3-Methoxy-4-methyl-9-xanthenone (**1e**) gave five acidic and one neutral product. The acidic products were found to be **2e**, **3e**, **4e**, **5e**, and **9b** which is identical with the product obtained from the reaction of **1b**. The neutral product was found to be **14b**, identical with the sample obtained from the oxidation of **1b** (Entry 7).

3-Methoxy-5-methyl-9-xanthenone (**1f**) yielded two carboxylated products, the structures of which were determined as **2f** and **6f**, being characterized as their methyl esters, and two acetoxymethyl-3-methoxy-5-methyl-9-xanthenones (**14f** and **15f**) substituted at the positions ortho to the methoxyl group (Entry 8).

Oxidation of 1-methoxy-3-methyl-9-xanthenone (**1g**) gave four acidic products (**2g**, **6g**, **11g**, and **13g**) and three neutral products (**14g**, **16g**, and **17g**) (Entry 9).

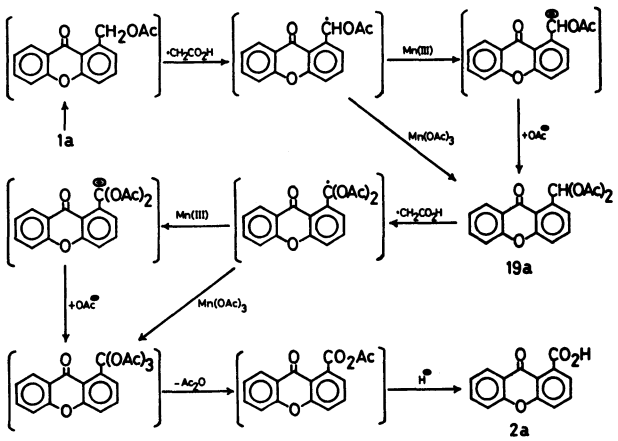
Carboxy derivatives were obtained in 3—30% yields and acetoxymethylated products in 2—25% yields. However, when **1g** was oxidized with eight equivalents of manganese(III) acetate, the yield of **14g** increased to 38% based on the **1g** consumed, while the other products were obtained only in small amounts.

It is known that the addition of potassium acetate to manganese(III) acetate oxidation increases the yield of the $-CH_2OAc$ product.[4] We studied the effect of added potassium acetate on the oxidation of **1b** (Entry 3). Contrary to our expectation the yields of the acetoxymethyl products did not increase, but two new carboxymethyl derivatives (**11b** and **12b**)were produced.

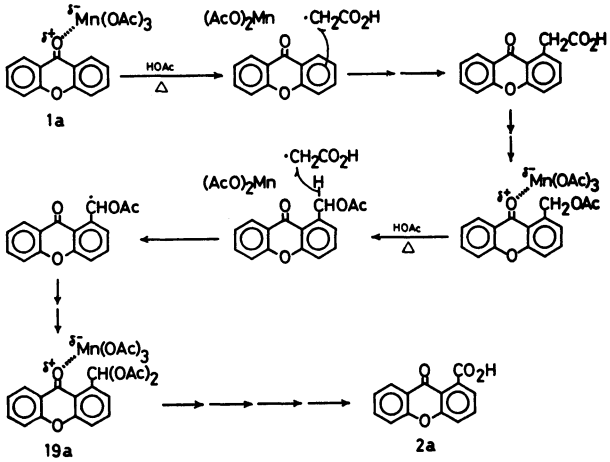
The reaction mechanism of acetoxymethylation of aromatic compounds has been established by the work of Heiba and his co-workers.[4] The carboxymethyl radical, $\cdot CH_2COOH$, which is somewhat electrophilic, attacks the positions of highest electron density. The CH_2COOH group is then converted, by oxidative decarboxylation, into the CH_2OAc group and hence these acetoxymethyl groups are situated at positions ortho to methoxyl or methyl groups. The reaction mechanism of the carboxylation, however, was not straightforward.

It is well known that the introduction of a carboxymethyl groups is the first step in the manganese(III) acetate oxidation of aromatic substrate of a higher ionization potential.[4] However, the introduction of a carboxyl group has been mentioned only by Dewar *et al.*[3] We wondered why carboxyl groups were introduced preferentially at the peri position. In the case of 9-xanthenones it is thought that the electron density of the peri position is lower because of the electron attraction by the carbonyl group, accordingly the rate of the attack at this position by the carboxymethyl radical should be slower. When a $\cdot CH_2COOH$ radical attacked at the position ortho to the methoxyl group, the oxidation reaction stopped at the stage of the $-CH_2OAc$ product. But when the $\cdot CH_2COOH$ radical attacked the peri position the oxidation did not stop at this stage, and further oxidation occurred to give a carboxyl product *via* a $-CH(OAc)_2$ compound.

To explain the fact mentioned above, we suggest that manganese(III) acetate forms a complex with the carbonyl function of 9-xanthenone and the complex subsequently decomposes to form a $\cdot CH_2COOH$ radical near the peri position. Then this position is attacked by the $\cdot CH_2COOH$ radical to form the $-CH_2COOH$ product, which is further oxidized to an acetoxymethyl compound. Another manganese(III) acetate complexes with the carbonyl group of 1-acetoxymethyl-9-xanthenones, and the second complex is decomposed again in acetic acid to yield another $\cdot CH_2COOH$ radical near the acetoxymethyl group. Consequently, the $-CH_2OAc$ compound is attacked by this radical and is then oxidized to give 1-diacetoxymethyl-9-xanthenone, which forms a third complex with manganese(III) acetate and is finally converted into the corresponding carboxy derivative *via* a similar oxidation sequence (Scheme 2). Aerial oxidation was not involved in the carboxylation, because the yields of carboxy derivatives scarcely changed as shown in



Scheme 1. Reaction mechanism of carboxylation of 9-xanthenone (**1a**) by manganese(III) acetate.



Scheme 2. Complexation between 9-xanthenone (**1a**) and manganese(III) acetate.

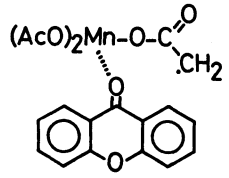


Fig. 2

the oxidation of **1c** under an atmosphere of nitrogen (Entry 5). It is also possible that the $\cdot CH_2COO-$ radical is formed on the manganese(III) acetate which is coordinated with 9-xanthenone as shown in Fig. 2, and then attacks the peri position intramolecularly.

The idea that a substrate will be oxidized *via* a complex with manganese(III) acetate has not been proposed previously. We can explain the regioselectivity of the carboxylation of the 9-xanthenone system only by assuming the complexation.

In order to investigate the carboxylation for other aromatic compounds, we carried out the oxidation of anthraquinone and benzophenone under the same reaction conditions. However, these compounds gave carboxymethyl, acetoxymethyl, and diacetoxymethy derivatives, and an aldehyde, but carboxylated products

were not detected.

It is known that **2a** is synthesized from 3-chlorophthalic acid and phenol in three steps and that it needs a long reaction time (yield: 25%).[14] On the other hand the reaction of **1a** with manganese(III) acetate gave **2a** (yield: 30%) in one step for a short reaction time. Therefore, it may be a convenient synthetic method for **2a** in some cases. The other carboxylated 9-xanthenones are new compounds and their synthetic methods are not known.

A small amount of 4- or 5-hydroxymethyl-9-xanthenones was also obtained. It seems that the corresponding acetoxymethyl-9-xanthenones were hydrolyzed to give the hydroxymethyl derivatives during the work-up.

Experimental

Measurements. ^{1}H-NMR spectra were recorded on a Hitachi Perkin-Elmer R-24 spectrometer with TMS as an internal standard. IR spectra were taken on a JASCO IRA-1 grating spectrometer. Mass spectra were measured on a Hitachi M-80 high resolution, and a JEOL JMS-01 SG-2 mass spectrometer, and a JMS-01 SG-2 instrument with direct inlet at 75 eV. HPLC analyses were performed on an Altex model 330/110A/153 isocratic liquid chromatograph equipped with a HY- ODS-5U column. Melting points were determined with a Yanagimoto micromelting point apparatus and were not corrected.

*Preparation of 9-Xanthenones (**1a**—**g**).* 9-Xanthenone (**1a**) was commercially available. The general proedure for the preparation of 9-xanthenones (**1b**, **c**, **f**, and **g**) was as follows.[8] A mixture of a benzoic acid (0.15 mol), a resorcinol (0.23 mol), fused zinc chloride (80 g), and phosphoryl chloride (100 ml) was heated for 3 h at 65 °C. The reaction mixture was poured into ice water (1.2 l) containing concd HCl (100 ml). The red gum which formed was decanted and triturated with an aqueous sodium hydrogencarbonate solution (800 ml). A benzophenone was formed and collected by filtration. The benzophenone (0.04 mol) and water (100 ml) were heated for 2.5 h at 210 °C in an autoclave, and the corresponding 9-xanthenone which was obtained was then methylated. **1e** was prepared from 2,4-dihydroxy-2′-methoxy-3-methylbenzophenone, which was heated with potassium hydroxide in ethanol followed by methylation.[9] **1d** was synthesized by the oxidation of 2-hydroxy-3′,4,4′-trimethoxybenzophenone with manganese(III) acetate.[11]

*Oxidation of 9-Xanthenones (**1a**—**g**).* The typical procedure for the oxidation of 9-xanthenones was as follows. To a mixture of the substrate (1 mmol) and acetic acid (25 ml) containing acetic anhydride (4 ml), the excess amount of manganese (III) acetate dihydrate[3] as shown in Table 1 was added. The mixture was then heated under reflux until the brown color of Mn(III) ion disappeared. After the removal of solvent *in vacuo*, the residue was triturated with 1 M (1 M=1 mol dm^{-3}) sulfuric acid (25 ml) and extracted with chloroform. The chloroform solution was washed with an aqueous sodium hydrogencarbonate solution (100 ml) and concentrated. The aqueous solution was acidified with concd hydrochloric acid and subsequently extracted with ethyl acetate. The ethyl acetate was removed and the acidic products were methylated with diazomethane in methanol. The neutral and esterified products, respectively, were separated on TLC (Wakogel B-10) with chloroform as the developing solvent, and recrystallized. The yields are summarized in Table 1.

*Oxidation Products of **1a**.* *1-Carboxy-9-xanthenone (**2a**)*: Mp 226—228 °C (EtOH) (lit,[10] mp 229—230 °C); IR (KBr) 1680 and 1720 (C=O), and 2500—3200 cm^{-1} (OH); NMR ($(CD_3)_2SO$) δ=7.39—8.26(7H, m, aromatic), and 13.0(1H, br. s, COOH).

*The Methyl Ester of **2a***: Mp 117 °C (MeOH); IR ($CHCl_3$) 1680 (C=O) and 1752 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=4.03 (3H, s, $COOCH_3$), and 7.04—8.16 (7H, m, aromatic). Found: C, 71.00; H, 4.12%. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96%.

*Dimethyl Ester of 1,8-Dicarboxy-9-xanthenone (**4a**)*: Mp 183—184 °C (MeOH); IR ($CHCl_3$) 1685 (C=O) and 1750 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.99 (6H, s, 2×$COOCH_3$), and 7.27—7.92 (6H, m, aromatic). Found: C, 65.12; H, 3.97%. Calcd for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87%.

*Methyl Ester of 1-Carboxy-4-hydroxymethyl-9-xanthenone (**9a**)*: Mp 185—186 °C (MeOH); IR(KBr) 1645 (C=O), and 1745 ($COOCH_3$), and 3300—3500 cm^{-1} (OH); NMR ($CDCl_3$) δ=3.5 (1H, br. s, OH), 4.05 (3H, s, $COOCH_3$), 4.99 (2H, s, $-CH_2-$), 7.04—8.35 (4H, m, aromatic), 7.19 (1H, d, J=7.8 Hz, $H_{(2)}$), and 7.80 (1H, d, J=7.8 Hz, $H_{(3)}$). Found: *m/e* 284.0685 (M^+). Calcd for $C_{16}H_{12}O_5$: M, 284.0685.

*Acetylation of the Methyl Ester of **9a***: The methyl ester of **9a** was treated with acetic anhydride in pyridine–acetic acid at room temperatrure overnight to afford the methyl ester of 4-acetoxymethyl-1-carboxy-9-xanthenone (**7a**); mp 84—85 °C (EtOH); IR ($CHCl_3$) 1675 and 1745 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.16 (3H, s, OAc), 4.02 (3H, s, $COOCH_3$), 5.46 (2H, s, $-CH_2-$), 7.2—8.3 (4H, m, aromatic), 7.28 (1H, d, J=7.8 Hz, $H_{(2)}$), and 7.76 (1H, d, J=7, 8 Hz, $H_{(3)}$).

*4-Acetoxymethyl-9-xanthenone (**14a**)*: Mp 118—119 °C (EtOH); IR ($CHCl_3$) 1673 (C=O) and 1745 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.14 (3H, s, OAc), 5.50 (2H, s, $-CH_2-$), and 7.25—8.39 (7H, m, aromatic). Found: *m/e* 268.0736 (M^+). Calcd for $C_{16}H_{12}O_4$: M, 268.0736.

*1-Diacetoxymethyl-9-xanthenone (**19a**)*: Mp 181—182 °C (EtOH); IR (KBr) 1686 (C=O), 1755 and 1768 cm^{-1} (OAc); NMR($CDCl_3$) δ=2.18(6H, s, 2×OAc), 7.24—8.43 (7H, m, aromatic), and 8.86 (1H, s, >CH–). Found: C, 66.25; H, 4.54%. Calcd for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32%.

*Oxidation Products of **1b**.* *Methyl Ester of 1-Carboxy-6-methoxy-9-xanthenone (**2b**)*: Mp 132—133 °C (MeOH); IR ($CHCl_3$) 1673 (C=O) and 1746 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.82 (3H, s, OCH_3), 4.03 (3H, s, $COOCH_3$), and 6.6—8.2 (6H, m, aromatic). Found: C, 67.48; H, 4.34%. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.26%.

*Methyl Ester of 1-Carboxy-4-hydroxymethyl-3-methoxy-9-xanthenone (**9b**)*: Mp 212—213 °C (MeOH); IR ($CHCl_3$) 1675 (C=O), 1750 ($COOCH_3$), and 3300—3600 cm^{-1} (OH); NMR ($CDCl_3$) δ=2.5 (1H, br. s, OH), 4.00 (3H, s, OCH_3), 4.05 (3H, s, $COOCH_3$), 5.08 (2H, s, $-CH_2-$), 6.97 (1H, s, $H_{(2)}$), and 7.2—8.3 (4H, m, aromatic); MS *m/e* 314 (M^+).

*Acetylation Product (Methyl Ester of **7b**) of the Methyl Ester of **9b***: Mp 174—175 °C (MeOH); IR ($CHCl_3$) 1670 and 1745 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.06 (3H, s, OAc), 3.97 (3H, s, OCH_3), 4.03 (3H, s, $COOCH_3$), 5.46 (2H, s, $-CH_2-$), 6.95 (1H, s, $H_{(2)}$), and 7.2—8.3 (4H, m, aromatic). Found: *m/e* 356.0895 (M^+). Calcd for $C_{19}H_{16}O_7$: M, 356.0896.

*Methyl Ester of 1-Carboxy-5-hydroxymethyl-6-methoxy-9-xanthenone (**10b**)*: Mp 198—199 °C (MeOH); IR ($CHCl_3$) 1675 (C=O), 1748 ($COOCH_3$), and 3300—3600 cm^{-1} (OH); NMR ($CDCl_3$) δ=2.4 (1H, br. s, OH), 3.98 (3H, s, OCH_3), 4.03 (3H, s, $COOCH_3$), 4.99 (2H, s, $-CH_2-$), 6.93 (1H, d, J=9.0 Hz, $H_{(7)}$), 7.15—7.65 (3H, m, aromatic), and 8.18 (1H, d, J=9.0 Hz, $H_{(8)}$); MS *m/e* 314 (M^+).

*Acetylation Product (Methyl Ester of **6b**) of the Methyl Ester of **10b***: Mp 199—200 °C (MeOH); IR ($CHCl_3$) 1675 and 1745 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.06 (3H, s, OAc), 3.96 (3H, s, OCH_3), 4.02 (3H, s, $COOCH_3$), 5.47 (2H, s, $-CH_2-$), 7.02 (1H, d, J=9.0 Hz, $H_{(7)}$), 7.23—7.87 (3H, m, aromatic), and 8.26 (1H, d, J=9.0 Hz, $H_{(8)}$). Found: *m/e* 356.0887 (M^+). Calcd for $C_{19}H_{16}O_7$: M. 356.0896.

*4-Acetoxymethyl-3-methoxy-9-xanthenone (**14b**)*: Mp 185—186 °C (EtOH); IR ($CHCl_3$) 1670 (C=O) and 1748 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.07 (3H, s, OAc), 3.97 (3H, s, OCH_3), 5.47 (2H, s, $-CH_2-$), 6.99 (1H, d, J=9.0 Hz, $H_{(2)}$), 7.20—8.35 (4H, m, aromatic), and 8.30 (1H, d, J=9.0 Hz, $H_{(1)}$). Found: C, 68.14; H, 4.90%. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73%.

*2-Acetoxymethyl-3-methoxy-9-xanthenone (**15b**)*: Mp 186—187 °C (EtOH); IR ($CHCl_3$) 1675 (C=O) and 1755 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.16 (3H, s, OAc), 3.95 (3H, s, OCH_3), 5.18 (2H, s, $-CH_2-$), 6.86 (1H, s, $H_{(4)}$), 7.24—8.36 (4H, m, aromatic), and 8.23 (1H, s, $H_{(1)}$). Found: C, 68.43; H, 4.77%. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73%.

*Oxidation Products of **1c**. Methyl Ester of 1-Carboxy-3,6-dimethoxy-9-xanthenone (**2c**)*: Mp 181 °C (MeOH); IR ($CHCl_3$) 1660 (C=O) and 1745 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.89 (6H, s, 2×OCH_3), 4.02 (3H, s, $COOCH_3$), 6.80 (1H, dd, J=10.2 and 2.4 Hz, $H_{(7)}$), 6.84 (2H, br. s, $H_{(2)}$ and $H_{(4)}$), 6.97 (1H, d, J=2.4 Hz, $H_{(5)}$), and 8.12 (1H, d, J=10.2 Hz, $H_{(8)}$). Found: C, 65.06; H, 4.77%. Calcd for $C_{17}H_{14}O_6$: C, 64.96; H, 4.49%.

*Methyl Ester of 1-Carboxy-3,6-dimethoxy-4-hydroxymethyl-9-xanthenone (**9c**)*: IR ($CHCl_3$) 1665 (C=O), 1750 ($COOCH_3$), and 3300—3600 cm^{-1} (OH); NMR ($CDCl_3$) δ=2.5 (1H, br. s, OH), 3.82 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 3.97 (3H, s, $COOCH_3$), 4.90 (2H, s, $-CH_2-$), 6.74 (1H, s, $H_{(2)}$), and 6.7—8.1 (3H, m, aromatic).

*Acetylation Product (Methyl Ester of **7c**) of the Methyl Ester of **9c***: Mp 178—180 °C (MeOH); IR ($CHCl_3$) 1670 and 1745 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.06 (3H, s, OAc), 3.90 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 4.01 (3H, s, $COOCH_3$), 5.43 (2H, s, $-CH_2-$), 6.85 (1H, s, $H_{(2)}$), and 6.8—8.2 (3H, m, aromatic). Found: *m/e* 386.0984 (M^+). Calcd for $C_{20}H_{18}O_8$: M, 386.1002.

*Methyl Ester of 4-Cardoxymethyl-3,6-dimethoxy-9-xanthenone (**11c**)*: Mp 196—197 °C (MeOH); IR ($CHCl_3$) 1660 (C=O), and 1750 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.72 (3H, s, $COOCH_3$), 3.90 (2H, s, $-CH_2-$), 3.95 (6H, s, 2×OCH_3), 6.92 (1H, dd, J=8.7 and 2.4 Hz, $H_{(7)}$), 7.02 (1H, d, J=10.2 Hz, $H_{(2)}$), 7.07 (1H, d, J=2.4 Hz, $H_{(5)}$), 8.25 (1H, d, J=8.7 Hz, $H_{(8)}$), and 8.29 (1H, d, J=10.2 Hz, $H_{(1)}$). Found: C, 65.78; H, 5.01%; *m/e* 328.0939 (M^+). Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91%; M, 328.0947.

*4-Acetoxymethyl-3,6-dimethoxy-9-xanthenone (**14c**)*: Mp 203 °C (EtOH); IR ($CHCl_3$) 1660 (C=O) and 1745 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.09 (3H, s, OAc), 3.90 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 5.44 (2H, s, $-CH_2-$), 6.90 (1H, dd, J=8.4 and 2.4 Hz, $H_{(7)}$), 6.96 (1H, d, J=9.0 Hz, $H_{(2)}$), 6.97 (1H, d, J=2.4 Hz, $H_{(5)}$), 8.14 (1H, d, J=8.4 Hz, $H_{(8)}$), and 8.30 (1H, d, J=9.0 Hz, $H_{(1)}$). Found: C, 65.88; H, 4.94%. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91%.

*2-Acetoxymethyl-3,6-dimethoxy-9-xanthenone (**15c**)*: Mp 188 °C (EtOH); IR ($CHCl_3$) 1670 (C=O) and 1755 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.16 (3H, s, OAc), 3.90 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 5.14 (2H, s, $-CH_2-$), 6.79 (1H, s, $H_{(4)}$), 6.87 (1H, dd, J=9.0 and 2.4 Hz, $H_{(7)}$), 6.96 (1H, d, J=2.4 Hz, $H_{(5)}$), 8.20 (1H, d, J=9.0 Hz, $H_{(8)}$), and 8.21 (1H, s, $H_{(1)}$). Found: C, 65.54; H, 4.98%. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91%.

*4,5-Bis(acetoxymethyl)-3,6-dimethoxy-9-xanthenone (**17c**) and 2,5-Bis(acetoxymethyl)-3,6-dimethoxy-9-xanthenone (**18c**)*: The mixture of **17c** and **18c** could not be completely separated. However, the NMR spectrum and HPLC study, and the result of elemental analysis supported the structures. Mp 234—235 °C (EtOH); IR ($CHCl_3$) 1665 (C=O) and 1750 cm^{-1} (OAc). NMR spectrum of **17c**; ($CDCl_3$) δ=2.07 (6H, s, 2×OAc), 3.98 (6H, s, 2×OCH_3), 5.47 (4H, s, 2×$-CH_2-$) 6.99 (2H, d, J=9.0 Hz, $H_{(2)}$ and $H_{(7)}$), and 8.27 (2H, d, J=9.0 Hz, $H_{(1)}$ and $H_{(8)}$). NMR spectrum of **18c**; ($CDCl_3$) δ=2.08 (3H, s, OAc), 2.14 (3H, s, OAc), 3.98 (6H, s, 2×OCH_3), 5.19 (2H, s, $-CH_2-$), 5.47 (2H, s, $-CH_2-$), 6.85 (1H, s, $H_{(4)}$), 6.99 (1H, d, J=9.0 Hz, $H_{(7)}$), 8.19 (1H, br. s, $H_{(1)}$) and 8.29 (1H, d, J=9.0 Hz, $H_{(8)}$). Found: C, 62.70; H, 5.15%. Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04%.

*Oxidation Products of **1d**. Methyl Ester of 1-Carboxy-2,3,6-trimethoxy-9-xanthenone (**2d**)*: Mp 197—198 °C (MeOH); IR ($CHCl_3$) 1665 (C=O) and 1755 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.87 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 3.98 (3H, s, OCH_3), 4.04 (3H, s, $COOCH_3$), 6.79 (1H, d, J=2.4 Hz, $H_{(5)}$), 6.86 (1H, dd, J=9.0 and 2.4 Hz, $H_{(7)}$), 6.86 (1H, s, $H_{(4)}$), and 8.14 (1H, d. J=9.0 Hz, $H_{(8)}$). Found: *m/e* 344.0892 (M^+). Calcd for $C_{18}H_{16}O_7$: M, 344.0896.

*Methyl Ester of 1-Carboxy-3,6,7-trimethoxy-9-xanthenone (**3d**)*: **12d** could not be completely separated from **11d**, but the NMR spectrum, high resolution mass spectrum, and HPLC study supported the structure. Mp 171—172 °C (MeOH); IR ($CHCl_3$) 1660 (C=O) and 1745 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.84 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.02 (3H, s, $COOCH_3$), 6.77 (1H, s, $H_{(5)}$), 6.80 (2H, br. s, $H_{(2)}$ and $H_{(4)}$), and 7.50 (1H, s, $H_{(8)}$). Found: *m/e* 344.0884 (M^+). Calcd for $C_{18}H_{16}O_7$: 344.0896.

*Methyl Ester of 1-Carboxy-4-hydroxymethyl-3,6,7-trimethoxy-9-xanthenone (**9d**)*: IR ($CHCl_3$) 1650 (C=O), 1745 ($COOCH_3$), and 3300—3600 cm^{-1} (OH); NMR ($CDCl_3$) δ=2.5 (1H, br. s, OH), 3.93 (3H, s, OCH_3), 3.97 (3H, s, OCH_3), 3.98 (3H, s, OCH_3), 4.03 (3H, s, $COOCH_3$), 4.89 (2H, s, $-CH_3-$), 6.82 (1H, s, $H_{(5)}$), 6.85 (1H, s, $H_{(2)}$), and 7.51 (1H, s, $H_{(8)}$); MS *m/e* 374 (M^+).

*Acetylation Product (Methyl Ester of **7d**) of the Methyl Ester of **9d***: Mp 262—263 °C (MeOH); IR ($CHCl_3$) 1660 and 1745 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.07 (3H, s, OAc), 3.92 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 3.99 (3H, s, OCH_3), 4.02 (3H, s, $COOCH_3$), 5.42 (2H, s, $-CH_2-$), 6.90 (2H, s, $H_{(2)}$ and $H_{(5)}$), and 7.54 (1H, s, $H_{(8)}$). Found: *m/e* 416.1115 (M^+). Calcd for $C_{21}H_{20}O_9$: M, 416.1107.

*Methyl Ester of 4-Carboxymethyl-2,3,6-trimethoxy-9-xanthenone (**11d**)*: Mp 198—200 °C (MeOH); IR ($CHCl_3$) 1660 (C=O) and 1755 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.69 (3H, s, $COOCH_3$), 3.92 (2H, s, $-CH_2-$), 3,93 (3H, s, OCH_3), 3.97 (3H, s, OCH_3), 3.99 (3H, s, OCH_3), 6.87 (1H, d, J=2.4 Hz, $H_{(5)}$), 6.87 (1H, dd, J=9.0 and 2.4 Hz, $H_{(7)}$), 7.61 (1H, s, $H_{(1)}$), and 8.23 (1H, d, J=9.0 Hz, $H_{(8)}$). Found: *m/e* 358.1059 (M^+). Calcd for $C_{19}H_{18}O_7$: M, 358.1053.

*5-Acetoxymethyl-2,3,6-trimethoxy-9-xanthenone (**14d**)*: Mp 233 °C (EtOH); IR ($CHCl_3$) 1655 (C=O) and 1745 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.08 (3H, s, OAc), 3.95 (6H, s, 2×OCH_3), 3.97 (3H, s, OCH_3), 5.40 (2H, s, $-CH_2-$), 6.85 (1H, s, $H_{(4)}$), 6.97 (1H, d, J=9.0 Hz, $H_{(7)}$), 7.54 (1H, s, $H_{(1)}$), and 8.26 (1H, d, J=9.0 Hz, $H_{(8)}$). Found: C, 63.54; H, 5.28%. Calcd for $C_{19}H_{18}O_7$:C, 63.68; H, 5.06%.

*2-Acetoxymethyl-3,6,7-trimethoxy-9-xanthenone (**15d**)*: Mp 208—209 °C (EtOH); IR ($CHCl_3$) 1660 (C=O) and 1750 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.12 (3H, s, OAc), 3.91 (3H, s, OCH_3), 3.94 (6H, s, 2×OCH_3), 5.12 (2H, s, $-CH_2-$), 6.74 (1H, s, $H_{(5)}$), 6.79 (1H, s, $H_{(4)}$), 7.53 (1H, s, $H_{(1)}$), and 8.16 (1H, s, $H_{(8)}$). Found: *m/e* 358.1043 (M^+). Calcd for $C_{19}H_{18}O_7$: M, 358.1053.

Oxidation Products of ***1e***. *Methyl Ester of 1-Carboxy-6-methoxy-5-methyl-9-xanthenone* (***2e***): Mp 184—185 °C (MeOH); IR ($CHCl_3$) 1665 (C=O) and 1748 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=2.31 (3H, s, CH_3), 3.92 (3H, s, OCH_3), 4.03 (3H, s, $COOCH_3$), 6.89 (1H, d, J=9.0 Hz, $H_{(7)}$), 7.15—7.82 (3H, m, aromatic), and 8.11 (1H, d, J=9.0 $H_{(8)}$). Found: C, 68.20; H, 4.92%. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73%.

*1-Carboxy-3-methoxy-4-methyl-9-xanthenone (**3e**)*: Mp 250 °C (EtOH); IR (KBr) 1610 and 1720 (C=O), and 2800—3100 cm^{-1} (OH); NMR ($(CD_3)_2SO$) δ=2.32 (3H, s, CH_3), 4.00 (3H, s, OCH_3), 7.17 (1H, s, $H_{(2)}$), 7.34—8.23 (4H, m, aromatic), and 13.0 (1H, br. s, COOH): MS *m/e* 284 (M^+). Found: C, 67.48; H, 4.40%. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.26%.

Methyl Ester of ***3e***: Mp 211—212 °C (MeOH); IR ($CHCl_3$) 1670 (C=O) and 1748 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=2.33 (3H, s, CH_3), 3.93 (3H, s, OCH_3), 4.02 (3H, s, $COOCH_3$), 6.86 (1H, s, $H_{(2)}$), and 7.15—8.29 (4H, m, aromatic). Found: C, 68.21; H, 4.77%. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73%.

Dimethyl Ester of 1,8-Dicarboxy-3-methoxy-4-methyl-9-xanthenone (***4e***): Mp 200—201 °C (MeOH); IR ($CHCl_3$) 1680 (C=O) and 1750 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=2.34 (3H, s, CH_3), 3.94 (3H, s, OCH_3), 3.96 (6H, s, 2×$COOCH_3$), 6.91 (1H, s, $H_{(2)}$), and 7.18—7.68 (3H, m, aromatic). Found: C, 64.01, H, 4.70%. Calcd for $C_{19}H_{16}O_7$: C, 64.04; H, 4.53%.

Dimethyl Ester of 5-Carboxymethyl-1-carboxy-3-methoxy-4-methyl-9-xanthenone (***5e***): Mp 179—180 °C (MeOH); IR ($CHCl_3$) 1675 (C=O) and 1750 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=2.37 (3H, s, CH_3), 3.68 (3H, s, $COOCH_3$), 3.93 (5H, s, $-CH_2-$ and OCH_3), 4.01 (3H, s, $COOCH_3$), 6.88 (1H, s, $H_{(2)}$), and 7.00—8.24 (3H, m, aromatic). Found: *m/e* 370.1051 (M^+). Calcd for $C_{20}H_{18}O_7$: M, 370.1053.

Oxidation Products of ***1f***. *Methyl Ester of 1-Carboxy-6-methoxy-4-methyl-9-xanthenone* (***2f***): Mp 193—194 °C (MeOH); IR ($CHCl_3$) 1670 (C=O) and 1755 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=2.45 (3H, s, CH_3), 3.81 (3H, s, OCH_3), 3.99 (3H, s, $COOCH_3$), 6.78 (1H, d, J=2.4 Hz, $H_{(5)}$), 6.83 (1H, dd, J=9.0 and 2.4 Hz, $H_{(7)}$), 7.11 (1H, s, J=7.8 Hz, $H_{(2)}$), 7.24 (1H, d, J=7.8 Hz, H $_{(3)}$),and 8.05 (1H, d, J=9.0 Hz, $H_{(8)}$). Found: C, 68.50; H, 4.82%. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73%.

Methyl Ester of 5-Acetoxymethyl-1-carboxy-6-methoxy-4-methyl-9-xanthenone (***6f***): Mp 152—153 °C (MeOH); IR ($CHCl_3$) 1675 (C=O) and 1747 cm^{-1} ($COOCH_3$ and OAc); NMR ($CDCl_3$) δ=2.06 (3H, s, OAc), 2.54 (3H, s, CH_3), 3.96 (3H, s, OCH_3), 3.99 (3H, s, $COOCH_3$), 5.44 (2H, s, $-CH_2-$), 6.98 (1H, d, J=9.0 Hz, $H_{(7)}$), 7.16 (1H, d, J=7.8 Hz, $H_{(2)}$), 7.48 (1H, d, J=7.8 Hz, $H_{(3)}$), and 8.22 (1H, d, J=9.0 Hz, $H_{(8)}$), Found: *m/e* 370.1043 (M^+). Calcd for $C_{20}H_{18}O_7$: M, 370.1053.

4-Acetoxymethyl-3-methoxy-5-methyl-9-xanthenone (***14f***): Mp 212 °C (EtOH); IR ($CHCl_3$) 1665 (C=O) and 1750 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.08 (3H, s, OAc), 2.49 (3H, s, CH_3), 3.99 (3H, s, OCH_3), 5.48 (2H, s, $-CH_2-$), 6.96 (1H, d, J=9.0 Hz, $H_{(2)}$), 6.84—8.20 (3H, m, aromatic), and 8.31 (1H, d, J=9.0 Hz, $H_{(1)}$). Found: C, 68.98; H, 5.24%. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16%.

2-Acetoxymethyl-3-methoxy-5-methyl-9-xanthenone (***15f***): Mp 187—188 °C (EtOH); IR ($CHCl_3$) 1670 (C=O) and 1755 cm^{-1} (OAc); NMR ($CDCl_3$), δ=2.16 (3H, s, OAc), 2.57 (3H, s, CH_3), 3.98 (3H, s, OCH_3), 5.24 (2H, s, $-CH_2-$), 6.96 (1H, s, $H_{(4)}$), 6.97—8.27 (3H, m, aromatic), and 8.28 (1H, s, $H_{(1)}$). Found: *m/e* 312.0993 (M^+). Calcd for $C_{18}H_{16}O_5$: M, 312.0998.

Oxidation Products of ***1g***. *Methyl Ester of 8-Carboxy-1-methoxy-3-methyl-9-xanthenone* (***2g***): Mp 186—187 °C (Benzene); IR ($CHCl_3$) 1670 (C=O) and 1750 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=2.39 (3H, s, CH_3), 3.96 (3H, s, OCH_3), 4.04 (3H, s, $COOCH_3$), 6.57 (1H, d, J=2.4 Hz, $H_{(2)}$), 6.79 (1H, d, J=2.4 Hz, $H_{(4)}$), and 7.14—7.80 (3H, m, aromatic). Found: C, 68.37; H, 4.91%. Calcd for $C_{17}H_{14}O_5$: C, 68.45, H, 4.73%.

Methyl Ester of 4-Acetoxymethyl-8-carboxy-1-methoxy-3-methyl-9-xanthenone (***6g***): Mp 197—198 °C (MeOH); IR ($CHCl_3$) 1675 (C=O) and 1750 cm^{-1} ($COOCH_3$ and OAc); NMR ($CDCl_3$) δ= 2.06 (3H, s, OAc), 2.44 (3H, s. CH_3), 3.97 (3H, s, OCH_3), 4.03 (3H, s, $COOCH_3$), 5.41 (2H, s, $-CH_2-$), 6.64 (1H, br. s, $H_{(2)}$), and 7.19—7.83 (3H, m, aromatic), Found: C, 64.60; H, 4.95%. Calcd for $C_{20}H_{18}O_7$: C, 64.86; H, 4.90%.

Methyl Ester of 5-Carboxymethyl-1-methoxy-3-methyl-9-xanthenone (***11g***): Mp 158—159 °C (EtOH); IR ($CHCl_3$) 1670 (C=O) and 1755 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=2.41 (3H, s. CH_3), 3.68 (3H, s, $COOCH_3$), 3.90 (2H, s, $-CH_2-$), 3.97 (3H, s, OCH_3), 6.58 (1H, d, J=2.4 Hz, $H_{(2)}$), 6.83 (1H, d, J=2.4 Hz, $H_{(4)}$), and 7.08—8.29 (3H, m, aromatic). Found: *m/e* 312.0994 (M^+). Calcd for $C_{18}H_{16}O_5$: M, 312.0998.

Methyl Ester of 4-Acetoxymethyl-5-carboxymethyl-1-methoxy-3-methyl-9-xanthenone (***13g***): Mp 184—185 °C (EtOH); IR ($CHCl_3$) 1670 (C=O) and 1755 cm^{-1} ($COOCH_3$ and OAc); NMR ($CDCl_3$) δ=2.08 (3H, s, OAc), 2.51 (3H, s, CH_3), 3.70 (3H, s, $COOCH_3$), 3.95 (2H, s, $-CH_2-$), 4.00 (3H, s, OCH_3), 5.38 (2H, s, $-CH_2-$), 6.67 (1H, br. s, $H_{(2)}$), and 7.15—8.32 (3H, m, aromatic). Found: *m/e* 384.1196 (M^+). Calcd for $C_{21}H_{20}O_7$: M, 384.1209.

4-Acetoxymethyl-1-methoxy-3-methyl-9-xanthenone (***14g***): Mp 149 °C (EtOH); IR ($CHCl_3$) 1660 (C=O) and 1745 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.07 (3H, s, OAc), 2.43 (3H, s, CH_3), 3.99 (3H, s, OCH_3), 5.41 (2H, s, $-CH_2-$), 6.59 (1H, s, $H_{(2)}$), and 7.2—8.3 (4H, m, aromatic). Found: C, 69,29; H, 5.28%. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16%.

3-Acetoxymethyl-1-methoxy-9-xanthenone (***16g***): Mp 174—175 °C (EtOH); IR $(CHCl)_3$ 1670 (C=O) and 1760 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.17 (3H, s, OAc), 3.99 (3H, s, OCH_3), 5.11 (2H, s, $-CH_2-$), 6.70 (1H, d, J=1.8 Hz, $H_{(2)}$), 6.98 (1H, d, J=1.8 Hz, $H_{(4)}$), and 7.20—8.35 (4H, m, aromatic), Found: *m/e* 298.0807 (M^+). Calcd for $C_{17}H_{14}O_5$: M, 298.0841.

4,5-Bis(acetoxymethyl)-1-methoxy-3-methyl-9-xanthenone (***17g***): Mp 174—175 °C (EtOH); IR ($CHCl_3$) 1675 (C=O) and 1755 cm^{-1} (OAc); NMR ($CDCl_3$) δ=2.06 (3H, s, OAc), 2,13 (3H, s, OAc), 2.54 (3H, s, CH_3), 4.00 (3H, s, OCH_3), 5.43 (4H, s, 2×$-CH_2-$), 6.69 (1H, s, $H_{(2)}$), and 7.19—8.34 (3H, m, aromatic). Found: *m/e* 384.1221 (M^+). Calcd for $C_{21}H_{20}O_7$: M, 384.1209.

Oxidation of ***1b*** *with Manganese(III) Acetate in the Presence of Potassium Acetate.* Potassium acetate (60 mmol) was dissolved in hot acetic acid (25 ml) containing acetic anhydride (4 ml). **1b** (1 mmol) and manganese(III) acetate dihydrate (12 mmol)were added to this mixture, which was heated under reflux until the brown color of Mn(III) ions disappeared. The resulting liquid was treated in a manner similar to that described above, giving **2b**, **9b**, **10b**, 4-carboxymethyl-3-methoxy-9-xanthenone (**11b**), 2-carboxymethyl-3-methoxy-9-xanthenone (**12b**), **14b**, and **15b**.

Methyl Ester of ***11b***: Mp 181 °C (MeOH); IR ($CHCl_3$) 1675 (C=O) and 1749 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=3.81 (3H, s, $COOCH_3$), 3.95 (2H, s, $-CH_2-$), 3.95 (3H, s, OCH_3), 6.96 (1H, d, J=9.0 Hz, $H_{(2)}$), 6.81—8.35 (4H, m, aromatic), and 8.29 (1H, d, J=9.0 Hz, $H_{(1)}$). Found: *m/e* 298.0863 (M^+). Calcd for $C_{17}H_{14}O_5$: M, 298.0841.

Methyl Ester of ***12b***: Mp 217—218 °C (MeOH); IR ($CHCl_3$) 1670 (C=O) and 1752 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$)

δ=3.71 (3H, s, $COOCH_3$), 3.71 (2H, s, $-CH_2-$), 3.93 (3H, s, OCH_3), 6.90 (1H, s, $H_{(4)}$), 7.22—8.38 (4H, m, aromatic), and 8.12 (1H, s, $H_{(1)}$). Found: *m/e* 298.0824 (M^+). Calcd for $C_{17}H_{14}O_5$: M, 298.0841.

Oxidation of ***1c*** *with Manganese(III) Acetate under an Atmosphere of Nitrogen.* **1c** (1 mmol) was oxidized with manganese(III) acetate dihydrate (12 mmol) under an atmosphere of nitrogen to give **2c** (mp 181 °C), **7c** (mp 178—180 °C), 1-carboxy-4,5-bis(acetoxymethyl)-3,6-dimethoxy-9-xanthenone (**8c**), **9c**, **11c** (mp 196—197 °C), **14c** (mp 203 °C), **15c** (mp 188 °C), **17c** and **18c** (mp 234—235 °C).

Methyl Ester of ***8c***: Mp 233—234 °C (MeOH); IR ($CHCl_3$) 1675 (C=O) and 1748 cm^{-1} ($COOCH_3$ and OAc); NMR ($CDCl_3$) δ=2.06 (6H, s, 2×OAc), 3.97 (6H, s, 2×OCH_3), 4.01 (3H, s, $COOCH_3$), 5.41 (4H, s, 2×$-CH_2-$), 6.87 (1H, s, $H_{(2)}$), 6.93 (1H, d, J=8.4 Hz, $H_{(7)}$), and 8.24 (1H, d, J=8.4 Hz, $H_{(8)}$). Found: *m/e* 458.1232 (M^+). Calcd for $C_{23}H_{22}O_{10}$: M, 458.1213.

Oxidation of Anthraquinone. Anthraquinone (2 mmol), manganese(III) acetate dihydrate (20 mmol), acetic acid (50 ml), and acetic anhydride (8 ml) were heated under reflux for 40 min under an atmosphere of nitrogen. The reaction mixture was treated in the manner described before to give 2-diacetoxymethylanthraquinone (2%): Mp 144—146 °C (EtOH); IR ($CHCl_3$) 1700 and 1775 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.15 (6H, s, 2×OAc), 7.27 (1H, s, >CH–), and 7.2—8.4 (7H, m, aromatic); MS *m/e* (rel intensity), 296 (14) ($M^+-CH_2=C=O$), 278 (26) (M^+-AcOH), 254 (24), 237 (100) ($R-\overset{+}{C}HOH$), 236 (74) ($R-CHO^+$), 235 (91) ($R-C=O^+$), and 208 (19) ($M^+-C_5H_6O_4$), 2-formylanthraquinone (3%): Mp 287—290 °C (EtOH); IR ($CHCl_3$) 1700 and 1725 cm^{-1} (C=O); NMR ($CDCl_3$) δ=7.2—8.5 (6H, m, aromatic), 8.77 (1H, br. s, $H_{(1)}$), and 10.16 (1H, s, CHO); Found: *m/e* 236.0493 (M^+), Calcd for $C_{15}H_8O_3$: M, 236.0474, and 1-carboxymethylanthraquinone (5%) characterized as its methyl ester: Mp 179—181 °C (MeOH); IR ($CHCl_3$) 1690 and 1745 cm^{-1} (C=O); NMR ($CDCl_3$) δ=3.74 (3H, s, $COOCH_3$), 4.22 (2H, s, $-CH_2-$), and 7.56—8.44 (7H, m, aromatic); Found: *m/e* 280.0738 (M^+), Calcd for $C_{17}H_{12}O_4$: M, 280.0736.

Oxidation of Benzophenone. Benzopenone (1 mmol) and manganese(III) acetate dihydrate (10 mmol) were heated under reflux for 39 min in acetic acid (25 ml) containing acetic anhydride (4 ml) to yield diacetoxymethylbenzophenone (The position of the substituent group could not be determined.) (4%): IR ($CHCl_3$) 1675 and 1770 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.14 (6H, s, 2×OAc), 7.61 (1H, s, >CH–), and 7.2—7.9 (9H, m, aromatic); Found: *m/e* 312.1014 (M^+), Calcd for $C_{18}H_{16}O_5$: M, 312.0998. Although some acetoxymethyl and carboxymethyl products were also formed, they could not be purified on TLC.

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