수용액에서 폴리에틸렌 글리콜 촉매에 의한
1, 8-Dioxo-octahydroxanthene 유도체의 다용도적이며 실용적인 합성

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A Versatile and Practical Synthesis of 1, 8-Dioxo-octahydroxanthene Derivatives Catalyzed by Polyethylene Glycol (PEG) in Water

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요 약. 수용액에서 다양한 알데히드 5, 5-dimethyl-1, 3-cyclohexanedione을 이용한 1, 8-Dioxo-octahydroxanthene 유도체의 편리하고 실용적인 합성이 촉매인 폴리에틸렌 글리콜(PEG)하에서 성공적으로 수행되었다. 간단한 work-up, 깨끗한 생성물, 높은 수율, 친환경적인 용매인 물의 사용은 이 방법의 특색이다.

주제어: Xanthenes, 폴리에틸렌 글리콜, 물

ABSTRACT. A convenient and practical synthesis of 1, 8-dioxo-octahydroxanthene derivatives using various aldehydes, 5, 5-dimethyl-1, 3-cyclohexanedione in water was successfully carried out in the presence of polyethylene glycol (PEG) as a catalyst. Simple work-up, clean products, high yields and water as a green solvent are the attractive features of this methodology.

Keywords: Xanthene, Polyethylene glycol, Water

INTRODUCTION

The multicomponent coupling reactions are emerging as a useful source for building-up complex molecules with maximum simplicity and several levels of structural diversity. The development of environmentally friendly procedures in chemical and pharmaceutical industries has become a crucial and demanding research area in modern organic chemistry.[1] Therefore, there has been considerable interest in green synthesis involving environmental benign catalyst and solvent. When solvent must be used, water is most acceptable in terms of cost and environmen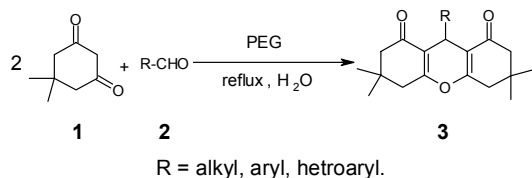tal impact. However, despite its large liquid range and extremely high specific heat capacity, it is frequently overlooked as a solvent for organic reactions. Most catalysts and reagents are deactivated or decomposed in water and in general, organic compounds are insoluble in water. Therefore, carrying out organic reactions in water poses 1important challenges in the area of reaction design. Rate enhancement of Diels-Alder reaction,[2] Claisen rearrangement,[3] the aldol condensation,[4] benzoin condensation[5] and many more organic transformations have been carried out in water.[6] Ideal synthesis involved preparation of target molecule in one step, in quantitative yield from readily available and inexpensive starting materials in resource effective and

environmentally acceptable process. Pioneer work by several research groups in this area has already established the versatility of one pot multicomponent coupling protocol as a powerful methodology.[7]

The most widely used procedures for the preparation of xanthene derivatives require organic solvents and long reaction time.[8] Very recently p-dodecylbenzenesulfonic acid has been reported as an acidic catalyst[9] for the synthesis of xanthene derivative. However, the synthesis of title compounds under neutral condition is not reported in the literature. Polyethylene glycol (PEG) has been used in number of organic reactions as a good phase transfer catalyst[10] so as to make organic materials soluble or form colloidal dispersion. The increasing demand for the development of new improved methods prompted us to employ PEG for the preparation of xanthene derivatives. In this paper we wish to highlight our results on the synthesis of xanthene derivatives using PEG as a catalyst under neutral conditions in aqueous medium (*Scheme* 1).

Various polyethylene glycols were tested for this transformation (*Table* 1).

The reaction of 4-hydroxybenzaldehyde with 5, 5-dimethyl-1, 3-cyclohexanedione was selected as a model reaction to test the feasibility of PEG used as a catalyst .We found that long chain PEG -6000

(*Table* 1, entry 6) was found to be more effective catalyst as compared to short chain catalysts (*Table* 1, Entries 1 ~ 5). 1, 8-dioxo-octahydroxanthene was formed in excellent yield (95%) using PEG-6000 as a catalyst under these reaction conditions.[12] Therefore it was decided to use PEG-6000 as the catalyst for further study.

The catalytic activity of PEG-6000 was then investigated with respect to the catalyst loading (*Table* 2).

Many experiments were carried out on a model reaction at 90 ^{o}C in an aqueous medium. We found that when less than 5 mol% of catalyst (PEG-6000) was applied; it resulted in lower yield of the product (*Table* 2, entries 2 ~ 5). Whereas use of more than 5 mol% did not improve the yield (*Table* 2, entries 7 ~ 8). When attempts were made to carry out the model reaction in absence of catalyst, we found that the intermediate dimethone (**5** *Scheme* 2) was obtained in 32% yield (*Table* 2, entry 1) and not the expected product **3a**. The catalyst could be recycled five times for the model reaction without significant loss of activity (*Table* 3).

Table 2. Optimization of molar ratio of catalyst for the model reaction

Entry	Mole %	Yield (%)[a]
1	0	32
2	1	48
3	2	70
4	2.5	75
5	3	79
6	5	95
7	10	96
8	15	95

[a]Yields listed refer to pure isolated product based on compound **1**.

R = alkyl, aryl, hetroaryl.

Scheme 1.

Table 1. Catalyst tested for the model reaction

Entry	Catalyst	Yield (%)[a]
1	PEG – 200	10
2	PEG – 400	24
3	PEG – 600	45
4	PEG – 2000	79
5	PEG – 4000	90
6	PEG – 6000	95

[a]Yields listed refer to pure isolated product based on compound **1**.

Table 3. Reuse of the catalyst for the model reaction

Entry	Recycle	Yield (%)[a]
1	1	95
2	2	94
3	3	92
4	4	90
5	5	89

[a]Yields listed refer to pure isolated product based on compound **1**.

We also examined the effect of the solvent on the model reaction (*Table* 4).

Water being a green solvent is obviously the best choice for these reactions.

We next investigated effect of reaction tempera-

ture on the yield and reaction time (*Table* 5).

When attempts were made to carry out the model reaction at room temperature (25 °C), the substrate was recovered almost (*Table* 5, entry 1) in quantitative amount. The rate of the model reaction could

Table 4. Solvents tried for the model reaction

Solvent	Yield (%)[a]
H_2O	95
MeCN	84
$CHCl_3$	65
EtOH	78

[a]Yields listed refer to pure isolated product based on compound **1**.

Table 5. Effect of temperature on yield and reaction time

Entry	Temperature (°C)	Reaction Time (h)	Yield (%)[a]
1	25	24	00
2	50	12	15
3	80	4.5	88
4	90	2.5	95
5	100	2.5	95

[a]Yields listed refer to pure isolated product based on compound **1**.

Table 6. PEG -6000 catalyzed synthesis of 1, 8- dioxo-octahydroxanthenes in water

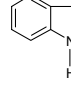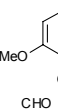| Entry	Aldehyde (2)	Time (h)	Yield (%)[a]	Entry	Aldehyde (2)	Time (h)	Yield (%)[a]
a		2.5	95	**i**		3.0	97
b		2.3	93	**j**		4.0	90
c		3.0	93	**k**		4.0	88
d		3.0	94	**l**		4.0	92
e		3.5	91	**m**		2.5	91
f		2.3	97	**n**		2.5	96
g		1.3	94	**o**		3.3	90
h		2.0	92				

[a]Yields listed refer to pure isolated product based on compound **1**.

markedly be increased, when the reaction temperature was elevated from 50 °C to 80 °C (*Table* 5, entries 2 ~ 3). When temperature was increase beyond 90 °C (*Table* 5, entry 5) no improvement in yield and reaction time was observed. So we thought to increase the reaction temperature to 90 °C to offer maximum yield of 95% in 2.5 h.

The results summarized in *Table* 6 indicate the generality of the methodology, because aliphatic, aromatic, heterocyclic and α, β-unsaturated aldehydes were converted into the corresponding 1,8-dioxo-octahydroxanthenes in quantitative yields in short reaction time as compared with reported methods. It is important to note that acid sensitive substrates (*Table* 6, entries m and n) and base sensitive substrates (*Table* 6, entries a and h) smoothly underwent condensation furnishing the corresponding 1, 8-dioxo-octahydroxanthenes in excellent yields under neutral condition. Even the dialdehydes (*Table* 6, entry k) underwent double condensation without any problem giving the corresponding bis-(1,8-dioxo-octahydroxanthenes) in good yield. (However, 4 equivalent amount of 5, 5-dimethyl-1, 3-cyclohexanedione **1** is required in this case). No Strongly obvious effect of electron and nature of substituents on the aromatic ring were observed. All aromatic aldehydes containing electron-withdrawing groups (such as nitro group, halide) or electron-donating groups (such as hydroxyl group, alkoxyl group) were employed and reacted well to give the corres-
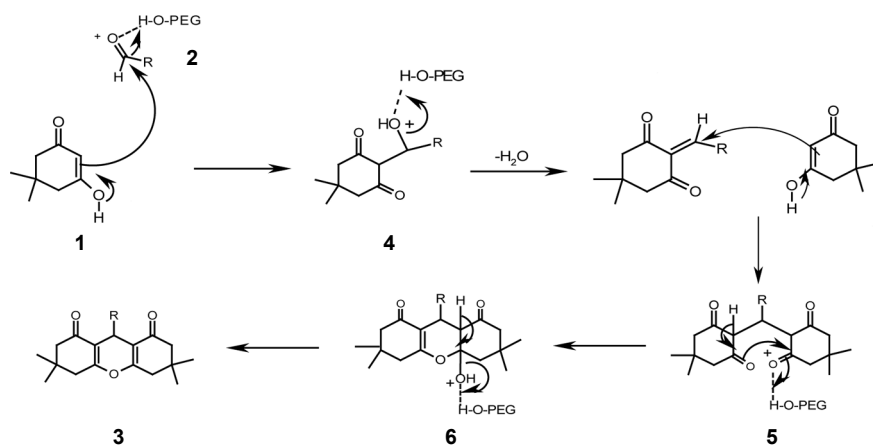
ponding product **3** in good to excellent yields under this reaction conditions. All the products are solid compounds and insoluble in water and the catalyst, PEG-6000 is soluble in water, therefore products are obtained in almost pure form by simple filtration of reaction mixture. The reaction completed smoothly in a short time at 90 °C under mild conditions. The tolerance of various functional groups under neutral reaction conditions, use of water as a green solvent, and short reaction time are important features of this protocol.

In conclusion, the present results demonstrate the efficiency of PEG-6000 as a catalyst for the preparation of ployfunctionalized 1, 8-dioxo-octahydroxanthene. Activated and inactivated aromatic, heterocyclic and aliphatic aldehydes under neutral reaction conditions involving an inexpensive and easily available catalyst and water as a green solvent furnished good to excellent yield of products in a very short reaction time. Almost pure products are obtained by simple filtration is noteworthy advantage as compared to the reported methods.

The *Scheme* 2 is as follow.

CONCLUSION

I Have develop a convenient and practical synthesis of 1, 8-dioxo-octahydroxanthene derivatives using various aldehydes, 5, 5-dimethyl-1, 3-cyclohexanedione in water using polyethylene glycol

Scheme 2.

(PEG) as a catalyst. The attractive features of this methodology are as follows:

1) Isolation of pure products by simple filtration of reaction mixture.

2) Use of water soluble, inexpensive and easily available catalyst (PEG 6000).

3) Use of water as green solvent.

4) Short reaction time and excellent yield of product.

5) Tolerance of various functional groups under neutral reaction condition. First time we are reporting neutral catalyst for this kind of synthesis.

EXPERIMENTAL

Typical Experimental Procedure: A mixture of 4-hydroxybenzaldehyde (0.122 g, 1 mmol), 5, 5-dimethyl-1, 3-cyclohexanedione (0.280 g, 2 mmol) and PEG-6000 (0.300 g, 5 mol %) in distilled water (15 mL) was stirred at 90 ^{o}C in a pre-heated oil bath. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature. The solid material was filtered, washed with water (2 × 10 mL) to furnish almost pure product. If necessary the products were further purified by recrystallization from ethanol. Spectral data of the compounds is given below:

3,3,6,6-Tetramethyl-9-(4-hydroxyphenyl)-1,8-dioxo-octahydroxanthene (3a). Mp 248 ^{o}C (lit.[9] 246～248 ^{o}C).

IR (KBr): 3350, 2980, 1795, 1725, 1699, 1640, 1520, 1360, 1345, 1260, 1233, 1201, 1195, 850, 843 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$,): δ = 0.94 (s, 6 H, 2 × CH$_3$), 1.06 (s, 6 H, 2 × CH$_3$), 2.13～2.25 (m, 8 H, 4 × CH$_2$), 4.42 (s, 1 H, H9), 7.07 (d, 2 H, J = 8.5 Hz, ArH), 7.96 (d, 2 H, J = 8.5 Hz, ArH).

Anal. Calcd for C$_{23}$H$_{26}$O$_4$: C, 75.38; H, 7.15. Found: C, 75.32; H, 7.08.

3,3,6,6-Tetramethyl-9-(dimethylaminophenyl)-1,8-dioxo-octahydroxanthene (3b). Mp 227 ^{o}C (lit.[9] 226～228 ^{o}C).

IR (KBr): 3035, 2985, 2190, 1680, 1665, 1580, 1499, 1454, 1235, 1190, 1040, 811, 743 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.94 (s, 6 H, 2 ×

CH$_3$), 1.06 (s, 6 H, 2 × CH$_3$), 2.13～2.25 (m, 8 H, 4 × CH$_2$), 2.94 (s, 6 H, N(CH$_3$)$_2$), 4.42 (s, 1 H, H9), 7.07 (d, 2 H, J = 8.5 Hz, ArH), 7.96 (d, 2 H, J = 8.5 Hz, ArH).

Anal. Calcd for C$_{25}$H$_{31}$NO$_3$: C, 76.36; H, 7.94; N, 3.56. Found: C, 76.32; H, 7.88; N, 3.60.

3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene (3c). Mp 230 ^{o}C (lit.[9] 228～229 ^{o}C).

IR (KBr): 2958, 2877, 1650, 1589, 1488, 1375, 1253, 1159, 1093, 1043, 887, 833 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.09 (s, 6 H, 2 × CH$_3$), 1.21 (s, 6 H, 2 × CH$_3$), 2.23～2.43 (m, 8 H, 4 × CH$_2$), 4.41 (s, 1 H, H9), 7.02 (d, 2 H, J = 8.0 Hz, ArH), 7.23 (d, 2 H, J = 8.0 Hz, ArH).

Anal. Calcd for C$_{23}$H$_{25}$ClO$_3$:C, 71.77; H, 6.55; Cl, 9.21. Found: C, 71.78; H, 6.50; Cl, 9.28.

3,3,6,6-Tetramethyl-9-(2,4-dichlorophenyl)-1,8-dioxooctahydroxanthene (3d). Mp 253～254 ^{o}C (lit.[9] 253～254 ^{o}C).

IR (KBr): 2960, 1720, 1614, 1467, 1388, 1288, 1230, 1185, 1141, 1068, 987, 860, 767 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.05 (s, 6 H, 2 × CH$_3$), 1.11 (s, 6 H, 2 × CH$_3$), 2.22～2.48 (m, 8 H, 4 × CH$_2$), 4.60 (s, 1 H, H9), 7.19～7.32 (m, 3 H, ArH).

Anal. Calcd for C$_{23}$H$_{24}$Cl$_2$O$_3$: C, 65.88; H, 5.71; Cl, 16.91. Found: C, 65.83; H, 5.74; Cl, 16.96.

3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-1,8-dioxo-octahydroxanthene (3e). Mp 170 ^{o}C (lit.[9] 168～170 ^{o}C).

IR (KBr): 2960, 2873, 1680, 1675, 1593, 1529, 1377, 1311, 1251, 1157, 1042, 842, 763, 732, 665 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.12 (s, 6 H, 2 × CH$_3$), 1.27 (s, 6 H, 2 × CH$_3$), 2.26～2.47 (m, 8 H, 4 × CH$_2$), 4.60 (s, 1 H, H9), 7.42 (s, 1 H, ArH), 7.88～7.95 (m, 3 H, ArH).

Anal. Calcd for C$_{23}$H$_{25}$NO$_5$: C, 69.89; H, 6.37; N, 3.54. Found: C, 69.94; H, 6.40; N, 30.50.

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene (3f). Mp 226～228 ^{o}C (lit.[9] 226～228 ^{o}C).

IR (KBr): 3028, 2980, 1650, 1591, 1512, 1373, 1301, 1249, 854 cm^{-1}.

^{1}H NMR (300MHz, CDCl$_3$): δ = 1.11 (s, 6 H, 2 ×

CH$_3$), 1.23 (s, 6 H, 2 × CH$_3$), 2.35～2.47 (m, 8 H, 4 × CH$_2$), 4.48 (s, 1 H, H9), 7.24 (d, 1 H, J = 8.1 Hz, ArH), 8.13 (d, 1 H, J = 8.1 Hz, ArH).

Anal. Calcd for C$_{23}$H$_{25}$NO$_5$: C, 69.86; H, 6.37; N, 3.54. Found: C, 69.83; H, 6.36; N, 3.48.

3,3,6,6-Tetramethyl-9-(3,4,5trimethoxyphenyl)-1,8-dioxo-octahydroxanthene (3g). Mp 72 °C.

IR (KBr): 2950, 1652, 1593, 1454, 1411, 1373, 1238, 1128, 885 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.12 (s, 6 H, 2 × CH$_3$), 1.1.24 (s, 6 H, 2 × CH$_3$), 2.35～2.41 (m, 8 H, 4 × CH$_2$), 3.75 (s, 6 H, 2 × OCH$_3$), 3.81 (s, 3 H, OCH$_3$), 4.45 (s, 1 H, H9), 6.34 (s, 2 H, ArH).

Anal. Calcd for C$_{26}$H$_{32}$O$_6$: C, 70.89; H, 7.32. Found: C, 70.85; H, 7.28.

3,3,6,6-Tetramethyl-9-(4-acetylaminophenyl)1,8dioxooctahydroxanthene (3h). Mp 222～224°C.

IR (KBr): 2962, 1666, 1595, 1541, 1448, 1375, 1313, 1263, 1159, 1041, 1018, 908, 835 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.09 (s, 6 H, 2 × CH$_3$), 1.22 (s, 6 H, 2 × CH$_3$), 2.15 (s, 3 H, NCOCH$_3$), 2.33～2.42 (m, 8 H, 4 × CH2), 4.45 (s, 1 H, H9), 7.28 (s, 1 H, NH),

7.11 (d, 2 H, J = 8.2 Hz, ArH), 7.41 (d, 2 H, J = 8.2 Hz, ArH).

Anal. Calcd for C$_{25}$H$_{29}$NO$_4$: C, 73.68; H, 7.17; N, 3.44. Found: C, 73.71; H, 7.21; N, 3.40.

3,3,6,6-Tetramethyl-9-(3,4-dioxymethylenephenyl)-1,8-dioxo-octahydroxanthene (3i). Mp 224 °C (lit.[9] 224～226 °C).

IR (KBr): 2956, 1668, 1591, 1490, 1444, 1371, 1307, 1236, 1157, 1122, 1039, 927, 864, 821, 750 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.09 (s, 6 H, 2 × CH$_3$), 1.21 (s, 6 H, 2 × CH$_3$), 2.24～2.45 (m, 8 H, 4 × CH$_2$), 4.45 (s, 2 H, H9), 5.91 (s, 2 H, OCH$_2$O), 6.56～6.69 (m, 3 H, ArH).

Anal. Calcd for C$_{24}$H$_{26}$O$_5$: C, 73.08; H, 6.64. Found: C, 73.05; H, 6.65.

3,3,6,6-Tetramethyl-9-(1-naphthyl)-1,8-dioxo-octahydroxanthene (3j). Mp 199～200 °C.

IR (KBr): 2980, 2956, 1668, 1490, 1444, 1371, 1307, 1236, 1157, 1122, 1039, 927, 864, 821, 750 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.06 (s, 6 H, 2 × CH$_3$), 1.11 (s, 6 H, 2 × CH$_3$), 2.27～2.46 (m, 8 H, 4 × CH$_2$), 4.25 (s, 2 H, H9), 7.54～7.86 (m, 4 H,

ArH), 7.91～8.14 (m, 3 H, ArH).

Anal. Calcd for C$_{27}$H$_{28}$O$_3$: C, 80.97; H, 7.05. Found: C, 81.01; H, 7.01.

(3K .2). Mp 288～290 °C.

IR (KBr): 2962, 1715, 1650, 1450, 1368, 1298, 1263, 1140, 1102, 1068,927, 850, 812 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$,): δ = 1.11 (s, 12 H, 4 × CH$_3$), 1.24 (s, 12 H, 4 × CH$_3$), 2.35～2.42 (m, 16 H, 8 × CH$_2$), 4.50 (s, 2 H, H9 and H9'), 7.23 (s, 4 H, ArH).

Anal. Calcd for C$_{40}$H$_{46}$O$_6$: C, 77.14; H, 7.44. Found: C, 77.18; H, 7.42.

3,3,6,6-Tetramethyl-9-(2-phenylethylene)-1,8-dioxo-octahydroxanthene (3l). Mp 176 °C (lit[9]. 175～177 °C).

IR (KBr): 3026, 2956, 1730, 1650, 1589, 1428, 1382, 1296, 1238, 1147, 1070, 968, 894, 842 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$,): δ = 1.07 (s, 6 H, 2 × CH$_3$), 1.25 (s, 6 H, 2 × CH$_3$), 2.31～2.42 (m, 8 H, 4 × CH2), 4.56 (s, 2 H, H9), 6.25～6.40 (m, 2 H, -CH = CH-), 7.01～7.28 (m, 5 H, ArH).

Anal. Calcd for C$_{25}$H$_{28}$O$_4$: C, 79.75; H, 7.50. Found: C, 79.81; H, 7.48.

3,3,6,6-Tetramethyl-9-(2-thiophene)-1,8-dioxo-octahydroxanthene (3m). Mp 176 °C.

IR (KBr): 2945, 1610, 1589, 1500, 1428, 1382, 1310, 1160, 955, 888 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.07(s, 6 H, 2 × CH$_3$), 1.25(s, 6 H, 2 × CH$_3$), 2.31～2.42 (m, 8 H, 4 × CH$_2$), 4.65 (s, 2 H, H9), 8.12～8.30 (m, 3 H, ArH).

Anal. Calcd for C$_{21}$H$_{24}$O$_4$S : C, 70.75; H, 6.75; S, 9.01. Found: C, 70.81; H, 6.76; S, 8.97.

3,3,6,6-Tetramethyl-9-(1 H-indol-3-yl)-1,8-dioxo-octahydroxanthene (3n). Mp 245～248 °C.

IR (KBr): 3224, 2949, 1672, 1616, 1525, 1377, 1228, 1132, 746 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.07 (s, 6 H, 2 × CH$_3$), 1.25 (s, 6 H, 2 × CH$_3$), 2.31～2.42 (m, 8 H, 4 × CH$_2$), 4.65 (s, 2 H, H9), 8.12～8.30 (m, 3 H, ArH).

Anal. Calcd for C$_{25}$H$_{27}$NO$_3$: C, 77.09; H, 6.99; N, 3.60. Found: C, 77.05; H, 7.01; N, 3.54.

3,3,6,6-Tetramethyl-9-(1-pently)-1,8-dioxo-octahydroxanthene (3o). Mp 117～119 °C.

IR (KBr): 2949, 2856, 1680, 1626, 1385, 1228,

1132, 850 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.99$ (t, 3 H, J = 6Hz, CH$_3$), 1.05 (s, 12 H, 4 × CH$_3$), 1.11~1.28 (m, 8 H, 4 × CH2), 1.92 (q, 2 H, J = 6 Hz, CH$_2$), 2.32~2.45 (m, 8 H, 4 × CH$_2$), 3.91 (t, 1 H, H9).

Anal. Calcd for C$_{22}$H$_{32}$O$_3$: C, 76.70; H, 9.34. Found: C, 76.65; H, 9.29.

2,2'-(4-hydroxyphenyl) methylene-bis (3-hydroxy-5, 5dimethyl-2-cyclohexene-1-one) (5). Mp 188 ^{o}C (lit^{11} 188~190 ^{o}C).

IR (KBr): 3344, 2980, 2510, 1699, 1480, 1355, 1240, 1233, 1195, 835 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.08$ (s, 6 H, 2 × CH$_3$), 1.16 (s, 6 H, 2 × CH$_3$), 2.20~2.35 (m, 8 H, 4 × CH$_2$), 5.45 (s, 1 H, H9), 7.10 (d, 2 H, J = 8.5 Hz, ArH), 8.01 (d, 2 H, J = 8.5 Hz, ArH), 9.88 (br s, 1 H, OH enol), 11.68 (br s, 1 H, OH enol).

Anal. Calcd for C$_{23}$H$_{28}$O$_5$: C, 71.85; H, 7.34. Found: C, 71.78; H, 7.36.

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