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# Scandium cation-exchanged montmorillonite catalyzed direct C-glycosylation of a 1,3-diketone, dimedone, with unprotected sugars in aqueous solution

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**Abstract**—The condensation of dimedone with unprotected sugars in aqueous solution in the presence of a catalytic amount of $Sc^{3+}$-montmorillonite ($Sc^{3+}$-mont) gave 9-hydroxyalkyl-3,3,6,6,-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-diones in good yields, while the use of $Sc(OTf)_3$ instead of $Sc^{3+}$-mont gave the hydroxyalkyl-6,7-dihydrobenzofuran-4(5*H*)-one derivatives in good yields. Furthermore, $Sc^{3+}$-mont could be recycled without inactivation.


*Keywords:* $Sc^{3+}$-mont; $Sc(OTf)_3$; Dimedone; C-Glycosylation; Water; Xanthene derivative; Benzofuran derivative; Recyclable

## 1. Introduction

Scandium(III) trifluoromethanesulfonate [$Sc(OTf)_3$], an environmentally benign, water-compatible catalyst, shows a stronger Lewis acidity than other rare earth metal trifluoromethanesulfonates.[1]

We recently developed a simple and direct C-glycosylation using $Sc(OTf)_3$ with unprotected sugars in aqueous media.[2] Most glycosylation reactions require protecting groups on the sugar and involve expensive substrates, precise reaction conditions, and complicated manipulations, resulting in overall product yields that are frequently low. The synthesis of phloroacetophenone mono- and bis-C-glycosides using this direct C-glycosylation and their use in the synthesis of naturally occurring flavonoid bis-C-glucopyranosides,[3] and the one-step synthesis of 1-deoxy-bis(3-indolyl)alditols[4] have been accomplished. When $Sc(OTf)_3$ was recycled and subsequently employed in the same reaction, however, its activity was decreased. In addition, the recycled catalyst was a mixture of catalyst and unreacted sugar owing to the fact that they were inseparable.[2] In an attempt to recycle $Sc(OTf)_3$ in these C-glycosylation reactions, we examined the use of an immobilized Sc(III) catalyst.

Some Sc(III)-immobilized catalysts have been developed.[5] Among them, Kaneda and co-workers[6] reported that $Sc^{3+}$-mont, prepared by cation exchange with a mixture of $Sc(OTf)_3$ and $Na^+$-mont in water, catalyzed the Michael addition of a 1,3-diketone to an enone in water or without solvent to afford Michael adducts in excellent yields, and was recyclable without inactivation. We employed this $Sc^{3+}$-mont instead of $Sc(OTf)_3$ in our direct C-glycosylation method.

## 2. Results and discussion

$Sc^{3+}$-mont was prepared by the method of Kaneda and co-workers, and the $Sc^{3+}$ content of the product was 0.370 mmol/g by ICP analysis (Ref. 6: 0.396 mmol/g).

We initially examined the C-glycosylation of phloroacetophenone, a key intermediate in flavonoid synthesis, with D-glucose in 1:9 $CH_3CN$–$H_2O$ at 80 °C using the

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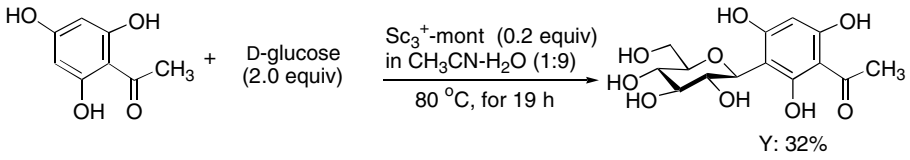


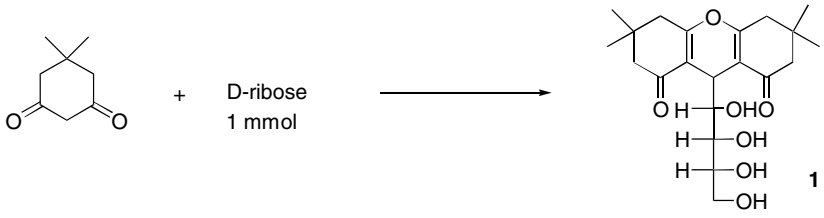

**Scheme 1.** $Sc^{3+}$-mont catalyzed C-glycosylation of phloroacetophenone with D-glucose.

prepared $Sc^{3+}$-mont.[2] However, contrary to our expectations, the maximum yield of the desired *C*-(β-D-glucopyranosyl)phloroacetophenone was 32%, lower than the 48% yield obtained using $Sc(OTf)_3$[2] (see Scheme 1).

We next examined the C-glycosylation of a more reactive 1,3-diketone (dimedone) with unprotected D-ribose to explore the utility of $Sc^{3+}$-mont (see Table 1). In an initial experiment, 2 mmol of dimedone and 1 mmol of D-ribose in the presence of 0.1 mmol of $Sc^{3+}$-mont was stirred in 3 mL of 2:1 $CH_3CN$–$H_2O$ at 50 °C for 3 days. The reaction proceeded more smoothly than the above C-glycosylation of phloroacetophenone to afford a condensation product comprising of 2 equiv of dimedone and 1equiv of ring-opened D-ribose, 3,3,6,6-tetramethyl-9-*C*-(D-*ribo*-tetritol-1-yl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**1**) in 45% yield, together with some other C-glycosides. The structure was verified by NMR analysis of the acetate. The structure of product **1** was similar to that of the product of condensation of 2 equiv of indole and 1 equiv of unprotected sugar using $Sc(OTf)_3$.[4] When the above reaction was carried out in only 3 mL of water, **1** was obtained in the same yield, 44%; however, the production of the other glycosides was suppressed to a considerable extent (entry 3). Since the $Sc^{3+}$-mont formed a gel when 3 mL of water was used and stirring was difficult, by increasing the volume of water used to 10 mL , it became possible to stir the reaction mixture more easily without gelation. The product yield was greatly improved, with yields up to 76%, and the amount of other glycosides produced was negligible (entry 4). When $Na^{+}$-mont was used instead of $Sc^{3+}$-mont as a catalyst under the same conditions as above, the reaction proceeded, but the yield of **1** was much lower (26%, entry 6). When the reaction temperature was increased to 60 °C, the yield was the same, but the reaction time could be shortened to 4 days (entry 7). After simple washing, the $Sc^{3+}$-mont was again available for use in the reaction (entries 5 and 8–11). Since even the fifth use gave **1** in the same 80% yield as the first run (entry 11), we conclude that the activity of $Sc^{3+}$-mont remained constant.

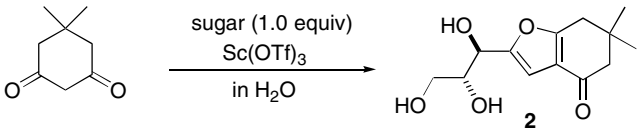
Interestingly, when $Sc(OTf)_3$ was used instead of $Sc^{3+}$-mont under the same reaction conditions, the reaction gave a benzofuran derivative, 2-(D-*erythro*-propanetriol-1-yl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (**2**), different from **1**, in 72% yield, which was the Knoevenagel condensation product of equal amounts of dimedone and D-ribose (Table 2, entry 1).[7] (The use of $CH_3CN$–$H_2O$ or EtOH–$H_2O$ as a solvent afforded a mixture of C-glycosides.) It is known that these furan or furanylfuran derivatives can be synthesized in good yield by the reaction of a 1,3-diketone, a 2,4-pentanedione and unprotected sugars in the presence of $ZnCl_2$,[7a] $CeCl_3$,[7b] or $Yb(OTf)_3$.[7c] When this reaction was carried out in the presence of 0.05 equiv of $Sc(OTf)_3$ at 75 °C for 1 day, the yield of **2** was increased to 86%

**Table 1.** C-Glycosylation of dimedone with D-ribose




| Entry | Dimedone (equiv) | Promoter (equiv) | Solvent | Temp (°C) | Time (day) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 2 | $Sc^{3+}$-mont (0.1) | $CH_3CN$–$H_2O$ (2:1) | 50 | 3 | 45.5 |
| 2 | 2 | $Na^{+}$-mont (0.1) | $CH_3CN$–$H_2O$ (2:1) | 50 | 2 | 27.6 |
| 3 | 2 | $Sc^{3+}$-mont (0.1) | $H_2O$ (3 mL) | 50 | 3 | 44.0 |
| 4 | 3 | $Sc^{3+}$-mont (0.1) | $H_2O$ (10 mL) | 50 | 7 | 76.0 |
| 5 | 3 | $Sc^{3+}$-mont (0.1) 2nd use | $H_2O$ (10 mL) | 50 | 7 | 78.9 |
| 6 | 3 | $Na^{+}$-mont (0.1) | $H_2O$ (10 mL) | 50 | 7 | 26.0 |
| 7 | 3 | $Sc^{3+}$-mont (0.1) 1st use | $H_2O$ (10 mL) | 60 | 4 | 77.8 |
| 8 | 3 | $Sc^{3+}$-mont (0.1) 2nd use | $H_2O$ (10 mL) | 60 | 4 | 80.7 |
| 9 | 3 | $Sc^{3+}$-mont (0.1) 3rd use | $H_2O$ (10 mL) | 60 | 4 | 77.7 |
| 10 | 3 | $Sc^{3+}$-mont (0.1) 4th use | $H_2O$ (10 mL) | 60 | 4 | 80.3 |
| 11 | 3 | $Sc^{3+}$-mont (0.1) 5th use | $H_2O$ (10 mL) | 60 | 4 | 79.8 |

**Table 2.** $Sc(OTf)_3$ catalyzed C-glycosylation of dimedone with D-ribose and D-glucose in water



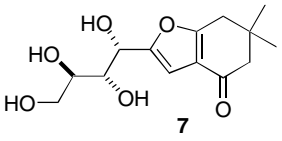
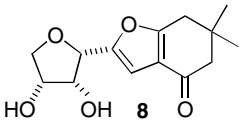
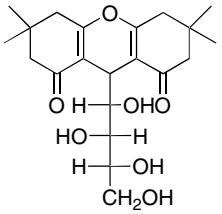
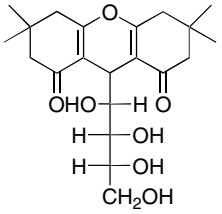
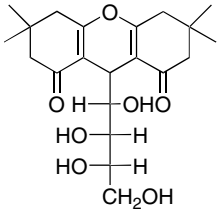
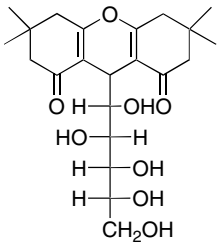

| Entry | Dimedone (equiv) | Sugar | $Sc(OTf)_3$ (equiv) | Temp (°C) | Time (day) | Product | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | 3.0 | D-Ribose | 0.1 | 60 | 4 | **2** | 72 |
| 2 | 1.5 | D-Ribose | 0.05 | 75 | 1 | **2** | 86 |
| 3 | 3.0 | D-Glucose | 0.2 | 60 | 7 |  **7** | 22 (**6**: 5) |
| 4 | 1.5 | D-Glucose | 0.1 | 70 | 3.5 |  **8** | 90 |

**Table 3.** $Sc^{3+}$-mont catalyzed C-glycosylation of dimedone with other pentoses and glucose

| Entry | Sugar (equiv) | $Sc^{3+}$-mont (equiv) | Temp (°C) | Time (day) | Product (%) | |
|---|---|---|---|---|---|---|
| 1 | D-Xylose | 0.1 | 60 | 4 |  | **3** (76) |
| 2 | D-Arabinose | 0.1 | 60 | 4 |  | **4** (79) |
| 3 | L-Arabinose | 0.1 | 60 | 4 |  | **5** (78) |
| 4 | D-Glucose | 0.1 | 60 | 4 |  | **6** (25) |
| 5 | D-Glucose | 0.1 | 70 | 2.5 | | **6** (32) |
| 6 | D-Glucose | 0.2 | 60 | 7 | | **6** (43) |

(entry 2). These different products produced under the same reaction conditions can be rationalized on the basis of a reaction mechanism proposed by Kaneda and co-workers,[6b] as follows: a dimedone and a D-ribose are coordinated to the Sc center in the silicate layers of $Sc^{3+}$-mont, and the successive carbon–carbon bond formation produces an intermediate. Another dimedone is then coordinated, and a second carbon–carbon bond formation between the intermediate and a dimedone produces **1**,[6b] while in the reaction using $Sc(OTf)_3$ in water, **2** is produced via carbon–carbon bond formation between a dimedone and a D-ribose molecule.

The glycosylation of dimedone using 0.1 equiv of $Sc^{3+}$-mont in water (10 mL/1 mmol of sugar) was applied to other pentoses, including D-xylose, D-arabinose, and L-arabinose, and the results are summarized in Table 3. The three pentoses also gave the desired xanthenes **3**, **4**, and **5** in yields of 76%, 79%, and 78%, respectively. Since a hexose, D-glucose showed a lower reactivity (25%) under the same reaction conditions (entry 4), a reaction using 0.2 equiv of $Sc^{3+}$-mont at 60 °C for 7 days gave **6** in a maximum yield of 43% (entry 6). D-Glucose also showed a similar low reactivity for a reaction using 0.2 equiv of $Sc(OTf)_3$ in 10 mL of $H_2O$ at 60 °C for 7 days, affording the desired benzofuran derivative, 2-(D-*arabino*-tetritol-1-yl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (**7**), in a low yield of 22%, along with other glycosides including 5% of **6** (Table 2, entry 3). When this reaction was carried out in the presence of 0.1 equiv of $Sc(OTf)_3$ at 70 °C for 3.5 days, the reaction proceeded smoothly to afford 2-(1,4-anhydro-D-*erythro*-tetrofuranosyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (**8**) in a yield of 90% without any other detectable glycosides. Compound **8** is a dehydration product between the C-1- and C-4-OH side-chain groups in **7** (entry 4).[7b,c] Finally, we applied this method to a gram-scale reaction. A suspension of 1.00 g of D-ribose, 2.78 g of dimedone, and 1.76 g of $Sc^{3+}$-mont (0.1 equiv of $Sc^{3+}$) in 100 mL of water was stirred vigorously at 60 °C for 4 days. After purification by silica-gel column chromatography, 2.15 g of pure **1** was obtained (82%). The above result verifies this synthetic method using $Sc^{3+}$-mont to be applicable to large-scale production.

## 3. Conclusion

$Sc^{3+}$-mont showed a weaker Lewis acidity in comparison to $Sc(OTf)_3$ in the direct C-glycosylation of phloroacetophenone with unprotected sugar in aqueous media. However, in the reaction of a 1,3-diketone with an

**Table 4.** Physicochemical data

| Compound no. | | Mp (°C) | $[\alpha]_D$ (MeOH) | IR ($cm^{-1}$) | Elemental analysis (C, H %) | FABMS $(M+H)^+$ |
|---|---|---|---|---|---|---|
| **1** | Colorless prisms | 133–134 | $[\alpha]_D^{22}$ +222 (*c* 1.025) | 3238, 2960, 1600, 1421, 1390, 1221, 1072, 1032 | Calcd for $C_{21}H_{30}O_7{\cdot}CH_3CH_2OH$: C, 62.71; H, 8.24. Found: C, 62.42; H, 8.56 | 395 |
| **2** | Colorless viscous oil | — | $[\alpha]_D^{22}$ +0.59 (*c* 1.015) | 3400, 2960, 2935, 2875, 1660, 1452, 1223, 1115, 1036 | Calcd for $C_{13}H_{18}O_5{\cdot}0.5H_2O$: C, 62.71; H, 8.24. Found: C, 59.44; H, 7.13 | 255 |
| **3** | Colorless prisms | 117–118 | $[\alpha]_D^{21}$ +181 (*c* 1.020) | 3398, 2956, 1616, 1392, 1225, 1117, 1072, 1032 | Calcd for $C_{21}H_{30}O_7{\cdot}0.4CH_3CH_2OH$: C, 63.41; H, 7.91. Found: C, 63.44; H, 8.10 | 395 |
| **4** | Colorless prisms | 123–124 | $[\alpha]_D^{22}$ −219 (*c* 1.035) | 3402, 2956, 1612, 1392, 1259, 1225, 1088, 1032 | Calcd for $C_{21}H_{30}O_7{\cdot}CH_3CH_2OH$: C, 62.71; H, 8.24. Found: C, 62.91; H, 8.17 | 395 |
| **5** | Colorless prisms | 119–120 | $[\alpha]_D^{21}$ +213 (*c* 1.055) | 3400, 2956, 1612, 1390, 1259, 1225, 1088, 1032 | Calcd for $C_{21}H_{30}O_7{\cdot}CH_3CH_2OH$: C, 62.71; H, 8.24. Found: C, 62.77; H, 8.14 | 395 |
| **6** | Colorless prisms | 163–164 | $[\alpha]_D^{21}$ +202 (*c* 1.025) | 3384, 2956, 1601, 1392, 1259, 1225, 1072, 1030 | Calcd for $C_{22}H_{32}O_8{\cdot}0.3CH_3CH_2OH$: C, 61.97; H, 7.78. Found: C, 62.12; H, 8.13 | 425 |
| **7** | Colorless prisms | 149–150 | $[\alpha]_D^{21}$ −18.5 (*c* 1.015) | 3433, 3319, 3265, 2970, 2929, 1658, 1450, 1410, 1296, 1082, 1028 | Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.39; H, 7.36 | 285 |
| **8** | Pale-yellow viscous oil | — | $[\alpha]_D^{22}$ −92.2 (*c* 1.000) | 3373, 2958, 2873, 1664, 1577, 1450, 1225, 1117, 1051, 1036 | Calcd for $C_{14}H_{18}O_5{\cdot}0.5CH_3OH$: C, 61.69; H, 7.14. Found: C, 61.80; H, 7.31 | 367 |

**Table 5.** $^1$H NMR data

| Chemical shifts (ppm) | Compound no. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **1** | **3** | **4** | **5** | **6** | | **2** | **7** | **8** |
| H-1′ | 4.46(dd) | 4.27(dd) | 4.40(dd) | 4.41(dd) | 4.17(dd) | H-1′ | 4.39(dd) | 4.78(dd) | 4.52(d) |
| H-2′ | 4.86(dd) | 4.62(dd) | 4.76(dd) | 4.76(dd) | 4.61(dd) | H-2′ | 3.66(m) | 3.53(dt) | 4.15(dd) |
| H-3′ | 3.62(dd) | 3.40(dd) | 3.16(dd) | 3.20(dd) | 3.59(dd) | H-3′a | 3.55(ddd) | 3.59(m) | 4.11(m) |
| H-4′ | 3.30(ddd) | 3.53(ddd) | 3.47(ddd) | 3.46(ddd) | 3.34(dd) | H-3′b | 3.45(ddd) | | |
| H-5′a | 3.56(dd) | 3.45(dd) | 3.59(dd) | 3.59(dd) | 3.46(ddd) | | | | |
| H-5′b | 3.44(dd) | 3.34(dd) | 3.41(dd) | 3.40(dd) | | H-4′a | | 3.49(ddd) | 4.03(dd) |
| H-6′a | | | | | 3.57(dd) | H-4′b | | 3.43(dt) | 3.63(dd) |
| H-6′b | | | | | 3.31(dd) | OH | 4.51(t) | 4.38(t) | 5.11(d) |
| | | | | | | | 4.72(d) | 4.61(d) | 5.14(d) |
| | | | | | | | 5.47(d) | 4.64(d) | |
| | | | | | | | | 5.18(d) | |
| (Xanthene moiety) | | | | | | (Benzofuran moiety) | | | |
| $CH_3$ | 0.96(s, ×2) | 0.96(s, ×2) | 0.97(s, ×2) | 0.97(s, ×2) | 0.95(s, ×2) | | | | |
| | 1.01(s, ×2) | 1.03(s, ×2) | 1.02(s) | 1.02(s) | 1.02(s) | | | | |
| | | | 1.03(s) | 1.03(s) | 1.03(s) | $CH_3$ | 1.06(s) | 1.06(s) | 1.06(s) |
| $CH_2$ | 1.88(d) | 1.91(d) | 1.90(d) | 1.92(d) | 1.90(d) | | 1.07(s) | 1.07(s) | 1.07(s) |
| | 2.01(d) | 2.03(d) | 2.02(d) | 2.02(d) | 2.05(d) | | 2.31(s) | 2.31(s) | 2.32(s) |
| | 2.18(d) | 2.20(d) | 2.18(d) | 2.18(d) | 2.21(d) | $CH_2$ | 2.77(s) | 2.76(s) | 2.79(s) |
| | 2.30(dd) | 2.29(dd) | 2.31(dd) | 2.29(dd) | 2.31(dd) | | | | |
| | | | | | | H-3 | 6.42(s) | 6.43(s) | 6.63(s) |
| *J* value (Hz) | | | | | | $J_{1',2'}$ | 7.3 | 7.3 | 7.3 |
| $J_{1,2}$ | 6.8 | 7.0 | 7.5 | 7.7 | 6.9 | $J_{1',OH}$ | 5.8 | 5.6 | |
| $J_{1,CH_2}$ | 2.2 | 2.2 | 1.2 | 2.3 | 2.0 | $J_{1',3}$ | | 1.2 | |
| $J_{2,3}$ | 2.2 | 5.6 | 1.2 | 1.1 | 6.9 | $J_{2',3'a}$ | 3.7 | 2.2 | 4.6 |
| $J_{3,4}$ | 9.0 | 3.7 | 8.5 | 8.9 | 2.0 | $J_{2',3'b}$ | 3.9 | | |
| $J_{4,5a}$ | 5.7 | 5.6 | 2.7 | 2.8 | 8.0 | $J_{2',OH}$ | 5.8 | 7.3 | 6.8 |
| $J_{4,5b}$ | 2.8 | 6.1 | 5.8 | 5.9 | | $J_{3'a,b}$ | 11.0 | | |
| $J_{5a,b}$ | 11.0 | 10.8 | 11.0 | 11.0 | 3.6 | $J_{3'OH}$ | 5.6 | 5.6 | 3.9 |
| $J_{5,6a}$ | | | | | 6.7 | $J_{3',4'a}$ | | 8.2 | 4.5 |
| $J_{5,6b}$ | | | | | 10.9 | $J_{3',4'b}$ | | 5.6 | 2.4 |
| $J_{6a,b}$ | 15.9 | 15.9 | 15.9 | 15.7 | 15.6 | $J_{4'a,b}$ | | 11.0 | 9.5 |
| $J_{CH_2}$ | 17.0 | 17.0 | 17.0 | 17.0 | 17.1 | $J_{4',OH}$ | | 5.6 | |

unprotected sugar in water, $Sc^{3+}$-mont had excellent catalytic activity and a different selectivity from $Sc(OTf)_3$, giving 9-hydroxyalkyl-3,3,6,6,-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione as the sole product in good yield, while $Sc(OTf)_3$ resulted in the production of hydroxyalkyl-6,7-dihydrobenzofuran-4(5*H*)-one derivatives. We are now exploring whether this difference in selectivity holds for other substrates.

## 4. Experimental

$Sc(OTf)_3$, purchased from Taiheiyo Kinzoku Co. Ltd., and $Na^+$-mont (Kunipia F, Kunimine Industry Co. Ltd.) were directly used without any further purification. The ICP analysis was carried out by using a Shimadzu ICPS 7000 instrument. The solvents used in this reaction were purified by distillation. Reactions were monitored by TLC on 0.25-mm Silica Gel F254 plates (E. Merck) using UV light, and a 7% ethanolic solution of phosphomolybdic acid with heat as a visualization agent. For separation and purification, flash column chromatography was performed on silica gel (230–400 mesh, Fuji-Silysia Co. Ltd., BW-300). Melting points were determined on a AS ONE ATM-01 melting point apparatus and are uncorrected. Optical rotations were recorded on a JASCO DIP-370 polarimeter. IR spectra were recorded on a Horiba FT-720 IR spectrometer in the form of KBr disks. NMR spectra were recorded on a Varian Inova 500 spectrometer using $Me_4Si$ as the internal standard. Mass spectral data were obtained by fast-atom bombardment (FAB) using glycerol as a matrix on a JEOL JMS-AX505HA instrument. Elemental analyses were performed on a Perkin–Elmer PE 2400 II instrument.

### 4.1. General procedure

**4.1.1. 3,3,6,6-Tetramethyl-9-*C*-(D-*ribo*-tetritol-1-yl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (1).** A suspension of dimedone (420 mg, 3 mmol), D-ribose (150 mg, 1 mmol), and $Sc^{3+}$-mont (270 mg, 0.1 mmol) in 10 mL of water was stirred at 60 °C for 4 days. The reaction mixture was cooled, filtered and washed with MeOH (3 mL). The filtrate was evaporated in vacuo. The residue was purified by silica-gel column chromatography (10:1 $CHCl_3$–MeOH). The crude product including **1** was recrystallized from ethanol to give pure

**Table 6.** $^{13}C$ NMR spectra

| Carbon no. | Compound no. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **1** | **3** | **4** | **5** | **6** | **2** | **7** | **8** |
| $CH_3$ | 27.33 | 27.33 | 27.48 | 27.51 | 27.34 | 27.84 | 27.82 | 27.77 |
| | 27.78(×2) | 27.71(×2) | 27.75(×2) | 27.77(×2) | 27.71(×2) | 27.91 | 27.93 | 27.89 |
| | 28.99 | 28.89 | 28.94 | 28.95 | 28.88 | | | |
| $CH_2$ | 31.43 | 31.52 | 31.46 | 31.46 | 31.51 | | | |
| | 31.51 | 33.72 | 33.65 | 33.65 | 35.03(×2) | 34.86 | 34.87 | 34.81 |
| | 33.69 | 35.00 | 34.58 | 34.60 | 37.20 | 36.31 | 36.26 | 36.25 |
| | 37.17 | 37.17 | 37.29 | 37.30 | | | | |
| C3,6 | 47.0(br, ×2) | 48.49(br, ×2) | 46.8(br, ×2) | 46.69(br, ×2) | 46.5(br, ×2) | 51.26(C6) | 51.26(C6) | 51.20(C6) |
| C1′ | 50.83 | 50.77 | 50.88 | 50.90 | 50.79 | 62.81 | 63.16 | 70.28 |
| C5′ or 6′ | 63.45 | 62.35 | 63.49 | 63.49 | 63.70 | 67.22 | 65.89 | 72.72 |
| C2′,3′,4′,5′ | 70.52 | 70.89 | 70.86 | 70.89 | 70.29 | 73.02 | 70.82 | 74.40 |
| | 71.35 | 72.02 | 72.11 | 72.13 | 71.26 | | 72.34 | 75.62 |
| | 90.57 | 90.06 | 88.67 | 88.70 | 71.34 | | | |
| | | | | | 90.96 | | | |
| | | | | | | 102.59(C3) | 101.99(C3) | 104.45(C3) |
| C8a,9a | 113.21 | 112.52 | 112.76 | 112.73 | 112.46 | 119.51(C3a) | 119.58(C3a) | 119.61(C3a) |
| | 113.98 | 113.41 | 114.06 | 114.09 | 113.27 | 157.16(C2) | 157.82(C2) | 153.94(C2) |
| C4a,10a | 175.95 | 175.64 | 175.89 | 175.79 | 175.54 | 165.38(C7a) | 165.07(C7a) | 166.39(C7a) |
| C1(C=O) | 192.08 | 192.24 | 192.20 | 192.11 | 192.14 | 193.45(C4, C=O) | 193.22(C4, C=O) | 193.18(C4, C=O) |

**1** (315 mg, 80%) as colorless prisms. The other xanthenes **3**, **4**, **5**, and **6** and benzofuran **7** were also isolated in the same manner. See Tables 1 and 3 for details and Tables 4–6 for physicochemical and NMR spectral data.

**4.1.2. 6,6-dimethyl-2-(D-*erythro*-propanetriol-1-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (2).** A solution of dimedone (420 mg, 3 mmol), D-ribose (150 mg, 1 mmol), and $Sc(OTf)_3$ (49 mg, 0.1 mmol) in 10 mL of water was stirred at 60 °C for 4 days. The reaction mixture was cooled, sodium phosphate (0.15 mmol) was added, and the solution was then evaporated in vacuo. The residue was purified by silica-gel column chromatography (10:1 $CHCl_3$–MeOH). This column chromatography operation was repeated to give pure **2** (183 mg, 72%) as a colorless, viscous oil. See Table 2 for details and Tables 4–6 for physicochemical and NMR spectral data.

**4.1.3. 6,6-Dimethyl-2-*C*-(α-D-*erythro*-tetrofuranosyl)-6,7-dihydrobenzofuran-4(5*H*)-one.** Pure compound **8**, isolated using the procedure mentioned in Section 4.1.2, was also obtained as a pale-yellow, viscous oil. See Table 2 for details and Tables 4–6 for physicochemical and NMR spectral data.

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