Synthesis of Precocenes With Ionoforic Groups

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Preparation of potential insect antijuvenile hormone agents with polyoxyethyl and glycosyl groups at C-8 position of the 2-*H*-chromene ring of precocenes is described.

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Our continuing interest in developing potential insect antijuvenile hormone agents, structurally related to precocenes, has recently led us to the synthesis of precocene analogs with a built-in crown ether moiety bridging the C-6 and C-7 positions of the 2-*H*-chromene ring to alter the absorption and transport properties of the natural products [1].

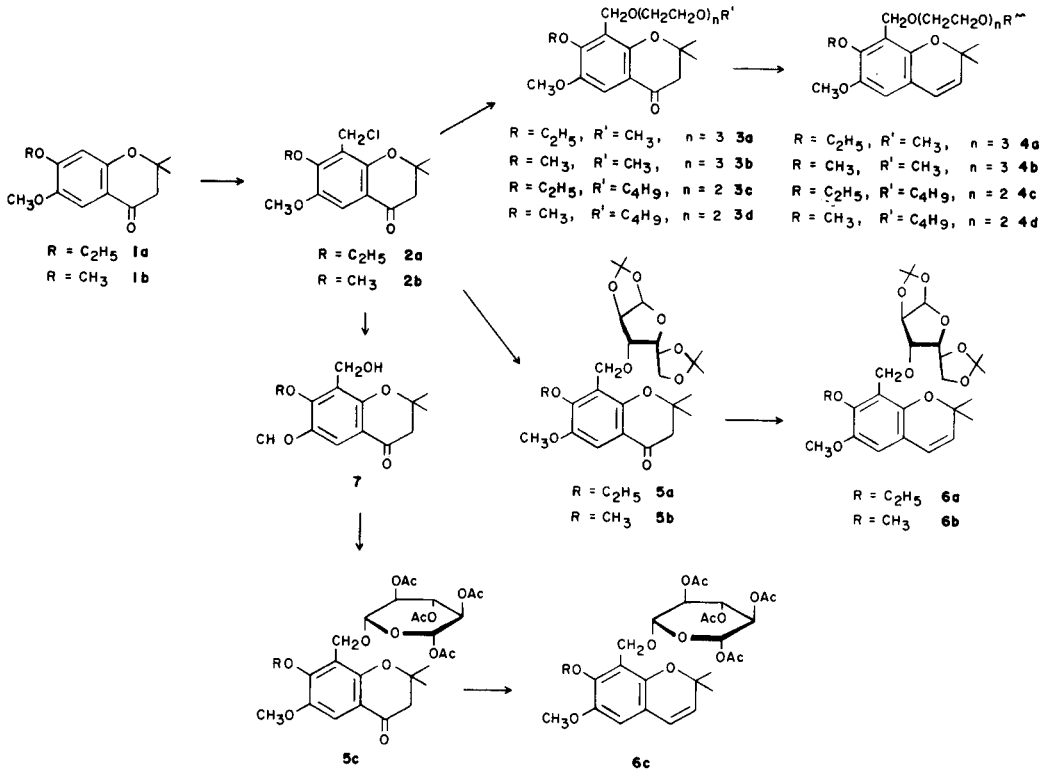
In this context, we describe in the present comnmunication the preparation of 8-polyoxyethyl and 8-glycosyl precocene analogs (**4** and **6**) by the sequence of reactions depicted in the Scheme.

The polyether chain is a common structural feature of several well known insecticide synergists, such as piperonyl butoxide, for which some insect juvenile hormone activity has also been indicated [2]. On the other hand, it has been reported that these moieties can facilitate the complexation with several cations [3] and the solubilization in water.

Likewise, the importance of the sugar residues for drug absorption and distribution is well established [4]. Recently, Slama has described the preparation of water soluble glycosydic juvenogens which exhibited insect juvenile hormone activity when ingested by insects and could protect the plants by systemic action [5].

Treatment of 6,7-dialkoxychroman-4-ones **1a** and **1b** with excess of methyl chloromethyl ether, in the presence of aluminium chloride as catalyst, afforded the corresponding 8-chloromethyl derivatives **2** (**2a**, 80%; **2b**, 83%). Reaction of these compounds with polyoxyethylenated alcohols under different basic conditions failed to give satisfactory yields of the desired 8-polyoxyethylene chromanones **3a-d**, which however, could be obtained in moderate

SCHEME I



yields (40-60%) by carrying out the above reactions at 170-180° in absence of solvent and using nickel bisacetylacetonate as catalyst. Final lithium aluminium reduction of **3** in refluxing diethyl ether afforded directly good yields (60-65%) of the corresponding 8-polyoxyethylenated chromenes **4a-d**.

On the other hand, reaction of **2a** and **2b** with 1,2,5,6-di-*O*-isopropylidene-α-D-glucofuranose in dry tetrahydrofuran in the presence of sodium hydride and tetrabutylammonium bromide as anionic activator [6] led to the formation of the corresponding 3-*O*-glucofuranosyl ethers **5a-b** in 25-42% yields, which under reduction with sodium borohydride in methanol and dehydration gave the corresponding 3-chromene derivatives **6a-b** in 55-60% yields.

Alternatively, application of the Koenigs-Knorr reaction by treatment of the hydroxymethyl derivative **7**, obtained in high yield by hydrolysis of **2a** with silver nitrate and water, with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide in dry chloroform solution in the presence of silver(I) oxide, calcium sulfate and iodine afforded 8-substituted chromanone **5c** (30%), which by reduction with sodium borohydride in methanol and dehydration gave the corresponding 3-chromene derivative **6c** in 52% yield.

Results of the biological activities of these compounds will be published elsewhere.

EXPERIMENTAL

8-Chloromethyl-7-ethoxy-2,2-dimethyl-6-methoxy-4-chromanone (**2a**).

Anhydrous aluminium trichloride (3.72 g, 0.02788 mole) was added within 10 minutes to a vigorously stirred solution of 7-ethoxy-6-methoxy-2,2-dimethylchroman-4-one (1.7 g, 0.0068 mole) in chloromethyl methyl ether (12 ml) at 5° under a dry nitrogen atmosphere. The mixture was stirred for 48 hours at room temperature poured into iced-water and extracted with methylene chloride (3 × 20 ml). The combined organic extracts were washed with saturated aqueous sodium chloride solution, dried (magnesium sulfate) and evaporated. The residue was purified by filtration through a silica gel column to yield **2a** (1.523 g, 80%) as a colorless thick oil; ir (chloroform): 1670 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.35 (1H, *H*-Ar, s), 4.68 (2H, CH_2Cl, s), 4.25 (2H, CH_2O, q, J = 7 Hz), 3.73 (3H, CH_3O, s), 2.70 (2H, CH_2C=O, s), 1.45 (6H, CH_3C, s), 1.40 (3H, CH_3C, t, J = 7 Hz).

Anal. Calcd. for $C_{15}H_{19}ClO_4$: C, 60.30; H, 6.70; Cl, 11.89. Found: C, 60.60; H, 6.40; Cl, 11.80.

8-Chloromethyl-2,2-dimethyl-6,7-dimethoxy-4-chromanone (**2b**).

Application of the same procedure described above using aluminium trichloride (2.31 g, 0.017 mole) 2,2-dimethyl-6,7-dimethoxychroman-4-one (1 g, 0.004 mole) and chloromethyl methyl ether (8 ml) afforded **2b** (0.996 g, 83%); ir (chloroform): 1670 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.40 (1H, *H*-Ar, s), 4.70 (2H, CH_2Cl, s), 4.03 (3H, CH_3O, s), 3.88 (3H, CH_3O, s), 2.65 (2H, CH_2C=O, s), 1.40 (6H, CH_3C, s).

Anal. Calcd. for $C_{14}H_{17}ClO_4$: C, 59.05; H, 5.90; Cl, 12.47. Found: C, 58.84; H, 6.01; Cl, 12.46.

7-Ethoxy-2,2-dimethyl-6-methoxy-8-(2',5',8',11'-tetraoxadodecyl)chroman-4-one (**3a**).

A mixture of **2a** (0.298 g, 0.001 mole), triethyleneglycol monomethyl ether (0.164 g, 0.001 mole) and nickel bisacetylacetonate (0.006 g, 0.000025 mole) was heated at 175-180° for 3 hours under a dry nitrogen atmosphere. The mixture was allowed to cool to room temperature, methylene chloride was added (30 ml) and the catalyst removed by filtration through silica gel. The solvent was eliminated at reduced pressure in a rotatory evaporator to give a residue (0.384 g) which was purified by preparative thin layer chromatography on silica gel (4 plates 20 × 20 × 0.25 cm thickness, 3:2 hexane:diethyl ether) to yield **3a** (0.164 g, 40%) as a thick colorless oil; ir (film): 1680, 1110 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.33 (1H, *H*-Ar, s), 4.57 (2H, CH_2OAr, s), 4.13 (2H, CH_2OAr, q, J = 7 Hz), 3.79 (3H, CH_3OAr, s), 3.60 (8H, CH_2O, s), 3.55 (4H, CH_2O), 3.30 (3H, CH_3O, s), 2.63 (2H, CH_2C=O, s), 1.40 (6H, CH_3C, s), 1.34 (3H, CH_3C, t, J = 7 Hz); ms: m/e 426 (M^+), 412 (M^+-CH_2), 411 (M^+-CH_3), 397 (M^+-C_2H_5), 396 (M^+-C_2H_6), 352 (M^+-$C_4H_{10}O$), 264 (M^+-$C_8H_{18}O_3$), 248 (M^+-$C_8H_{18}O_4$), 204 (M^+-$C_{10}H_{22}O_5$).

Anal. Calcd. for $C_{22}H_{34}O_7$: C, 61.97; H, 7.98. Found: C, 62.22; H, 7.73.

2,2-Dimethyl-6,7-dimethoxy-8-(2',5',8',11'-tetraoxadodecyl)chroman-4-one (**3b**).

Application of the same procedure described above using **2b** (0.358 g, 0.00125 mole), triethyleneglycol monomethyl ether (0.21 g, 0.00125 mole) and nickel bisacetylacetonate (0.006 g, 0.000025 mole) afforded **3b** (0.3 g, 58%); ir (chloroform); 1680, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.35 (1H, *H*-Ar, s), 4.60 (2H, CH_2Ar, s), 3.95 (3H, CH_3OAr, s), 3.85 (3H, CH_3OAr, s), 3.65 (8H, CH_2O, s), 3.60 (4H, CH_2O, s), 3.35 (3H, CH_3O, s), 2.65 (2H, CH_2C=O, s), 1.45 (6H, CH_3C, s).

Anal. Calcd. for $C_{21}H_{32}O_8$: C, 61.15; H, 7.82. Found: C, 61.22; H, 7.97.

7-Ethoxy-2,2-dimethyl-6-methoxy-8-(2',5',8'-trioxadodecyl)chroman-4-one (**3c**).

Application of the same procedure described above using **2a** (0.298 g, 0.001 mole), diethyleneglycol monobutyl ether (0.163 g, 0.001 mole) and nickel bisacetylacetonate (0.006 g, 0.000025 mole) afforded **3c** (0.162 g, 39%); ir (film): 1680, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.35 (1H, *H*-Ar, s); 4.60 (2H, CH_2OAr, s), 4.18 (2H, CH_2OAr, q, J = 7 Hz), 3.85 (3H, CH_3O, s), 3.65 (4H, CH_2O, s), 3.40-3.65 (6H, CH_2C), 2.60 (2H, CH_2C=O, s), 1.45 (13H, CH_3C, s), 1.40 (3H, CH_3C, t, J = 7 Hz).

Anal. Calcd. for $C_{23}H_{36}O_7$: C, 65.07; H, 8.55. Found: C, 65.10; H, 8.61.

2,2-Dimethyl-6,7-dimethoxy-8-(2',5',8'-trioxadodecyl)chroman-4-one (**3d**).

Application of the same procedure described above using **2b** (0.284 g, 0.001 mole), diethyleneglycol monobutyl ether (0.163 g, 0.001 mole) and nickel bisacetylacetonate (0.006 g, 0.000025 mole) afforded **3d** as a thick colorless oil (0.2 g, 49%); ir (chloroform): 1680, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.45 (1H, *H*-Ar, s), 4.60 (2H, CH_2Ar, s), 3.93 (3H, CH_3O, s), 3.83 (3H, CH_3O, s), 3.65 (4H, CH_2O, s), 3.35-3.60 (6H, CH_2C), 2.65 (2H, CH_2C=O, s), 1.43 (13H, CH_3C, s).

Anal. Calcd. for $C_{22}H_{34}O_7$: C, 64.37; H, 8.35. Found: C, 64.22; H, 8.15.

7-Ethoxy-2,2-dimethyl-6-methoxy-8-(2',5',8',11'-tetraoxadodecyl)chromene (**4a**).

Lithium aluminium hydride (0.014 g, 0.00038 mole) was added to a stirred solution of **3a** (0.164 g, 0.00038 mole) in dry diethyl ether (3 ml). The mixture was stirred for ten minutes at room temperature and excess hydride was destroyed by adding ethyl acetate dropwise. The precipitate was removed by filtration and the filtrate evaporated to give a mixture (0.114 g) of **4a** and the corresponding chromanol. The mixture was heated at 100° under reduced pressure yielding **4a** alone (0.094 g, 58%); ir (chloroform): 1460 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 6.53 (1H, *H*-Ar, s), 6.23 (1H, C*H*=C, d, J = 10 Hz), 5.53 (1H, C*H*=C, d, J = 10 Hz), 4.60 (2H, CH_2OAr, s), 4.05 (2H, CH_2OAr, q, J = 7 Hz), 3.78 (3H, CH_3OAr, s), 3.63 (8H, CH_2O, s), 3.58 (4H, CH_2O), 3.35 (3H, CH_3O, s), 1.40 (6H, CH_3C, s), 1.38 (3H, CH_3C, t, J = 7 Hz).

Anal. Calcd. for $C_{22}H_{34}O_7$: C, 64.37; H, 8.35. Found: C, 64.46; H, 8.65.

2,2-Dimethyl-6,7-dimethoxy-8-(2',5',8',11'-tetraoxadodecyl)chromene (**4b**).

Application of the same procedure described above using lithium aluminium hydride (0.028 g, 0.00076 mole) and **3b** (0.313 g, 0.00076 mole) in dry diethyl ether (3 ml) afforded **4b** (0.181 g, 60%); ir (chloroform): 1460,

1130 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 6.55 (1H, *H*-Ar, s), 6.23 (1H, CH=C, d, J = 10 Hz), 5.53 (1H, CH=C, d, J = 10 Hz), 4.60 (2H, CH_2Ar, s), 3.85 (3H, CH_3OAr, s), 3.78 (3H, CH_3OAr, s), 3.65 (8H, CH_2O, s), 3.55 (4H, CH_2O), 3.33 (3H, CH_3O, s), 1.40 (6H, CH_3C, s).

Anal. Calcd. for $C_{21}H_{32}O_7$: C, 63.62; H, 8.14. Found: C, 63.54; H, 8.01.

7-Ethoxy-2,2-dimethyl-6-methoxy-8-(2',5',8'-trioxadodecyl)chromene (**4c**).

Application of the same procedure described above using lithium aluminium hydride (0.014 g, 0.00038 mole), and **3c** (0.162 g, 0.00038 mole) in dry diethyl ether (3 ml) afforded **4c** (0.100 g, 64.5%); ir (chloroform): 1460, 1130 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 6.55 (1H, *H*-Ar, s), 6.22 (1H, C*H*=C, d, J = 10 Hz), 5.51 (1H, C*H*=C, d, J = 10 Hz), 4.60 (2H, CH_2Ar, s), 4.05 (2H, CH_2OAr, q, J = 7 Hz), 3.75 (3H, CH_3OAr, s), 3.62 (4H, CH_2O, s), 3.30-3.60 (6H, CH_2C), 1.40 (13H, CH_3C), 1.38 (3H, CH_3C, t, J = 7 Hz).

Anal. Calcd. for $C_{23}H_{36}O_6$: C, 67.62; H, 8.88. Found: C, 67.98; H, 8.51.

2,2-Dimethyl-6,7-dimethoxy-8-(2',5',8'-trioxadodecyl)chromene (**4d**).

Application of the same procedure described above using lithium aluminium hydride (0.019 g, 0.00049 mole), and **3d** (0.2 g, 0.00049 mole) in dry diethyl ether (3 ml) afforded **4d** (0.120 g, 62%); ir (chloroform): 1470, 1110 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 6.55 (1H, *H*-Ar, s), 6.23 (1H, C*H*=C, d, J = 10 Hz), 5.51 (1H, C*H*=C, d, J = 10 Hz), 4.60 (2H, CH_2Ar, s), 3.85 (3H, CH_3OAr, s), 3.78 (3H, CH_3OAr, s), 3.65 (4H, CH_2O, s), 3.30-3.70 (6H, CH_2C), 1.40 (13H, CH_3C).

Anal. Calcd. for $C_{22}H_{34}O_6 \cdot H_2O$: C, 64.07; H, 8.70. Found: C, 64.50; H, 8.35.

7-Ethoxy-8-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl)-methyl-2,2-dimethyl-6-methoxychroman-4-one (**5a**).

Sodium hydride (0.103 g, 50%, 0.00213 mole), was added carefully to a stirred solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (0.550 g, 0.00213 mole) in dry tetrahydrofuran (5 ml) at 5° under a dry nitrogen atmosphere. When the medium was homogeneous tetra-*n*-butyl ammonium bromide (0.009 g, 0.000002 mole), iodine (0.003 g) and **2a** (0.637 g, 0.00213 mole) were added. The mixture was stirred at room temperature for 48 hours and florisil (**3g**) was added, the solvent evaporated at reduced pressure. The florisil was eluted with chloroform, and the eluate was evaporated to give a residue (0.620 g) which was purified by thin layer chromatrography (3 plates, 20 × 40 × 0.25 cm, eluted with chloroform) to give **5a** (0.411 g, 37%) as a thick colorless oil; ir (film): 1680, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.40 (1H, *H*-Ar, s), 5.88 (1H, CH_2O), 4.55-4.80 (2H, CH_2O), 3.80-4.40 (8H, C*H*O), 3.85 (3H, CH_3O, s), 2.70 (2H, CH_2C=O, s), 1.10-1.70 (21H, CH_3C); ms: m/e 522 (M^+), 507 (M^+-CH_3), 464 (M^+-C_4H_{10}), 424 (M^+-$C_5H_6O_2$), 395 (M^+-$C_7H_{11}O_2$), 320 (M^+-$C_{10}H_{18}O_4$), 263 (M^+-$C_{12}H_{19}O_6$), 250 (M^+-$C_{13}H_{20}O_6$), 235 (M^+-$C_{14}H_{23}O_6$), 297 (M^+-$C_{16}H_{27}O_6$).

Anal. Calcd. for $C_{37}H_{58}O_{10}$: C, 62.06; H, 7.33. Found: C, 62.30; H, 7.39.

8-(1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl)methyl-2,2-dimethyl-6,7-dimethoxychroman-4-one (**5b**).

Application of the same procedure as described above using **2b** (0.568 g, 0.0019 mole), 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (0.226 g, 0.00045 mole), sodium borohydride (0.017 g, 0.00045 mole) in methanol (3 ml) afforded **4f** (0.193 g, 87%); ir (chloroform): 1460, 1430 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 6.55 (1H, *H*-Ar, s), 6.23 (1H, C*H*=C, d, J = 10 Hz), 5.90 (1H, O-C*H*-O, d), 5.55 (1H, C*H*=C, d, J = 10 Hz), 4.55-4.80 (2H, CH_2O), 3.80-4.40 (8H, CH_2O), 3.70 (3H, CH_3O, s), 1.20-1.70 (21H, CH_3O).

Anal. Calcd. for $C_{26}H_{36}O_9$: C, 63.40; H, 7.37. Found: C, 63.15; H, 7.46.

8-Hydroxymethyl-2,2-dimethyl-6,7-dimethoxychroman-4-one (**7**).

Silver nitrate (0.194 g) was added to a stirred solution of **2b** (0.325 g, 0.00114 mole) in acetone/water 1:1 (9 ml). The mixture was stirred at room temperature for 6 hours, extracted with diethyl ether (3 × 10 ml). The organic layers were washed with water, dried and evaporated, affording **7** (0.228 g, 78%); ir (chloroform): 3400, 1650, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.35 (1H, *H*-Ar, s), 4.75 (2H, CH_2O, s), 3.95 (3H, CH_3O, s), 3.85 (3H, CH_3O, s), 2.70 (2H, CH_2C=O, s), 2.30 (1H, O*H*, s), 1.45 (6H, CH_3C, s).

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.25; H, 7.20.

8-(2',3',4',6'-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2,2-dimethyl-6,7-dimethoxychroman-4-one (**5c**).

Silver oxide (0.114 g, 0.00054 mole), dry magnesium sulfate (drierite, 0.383 g) and iodine (0.183 g) were added over a stirred solution of **7** (0.145 g, 0.00054 mole) in dry chloroform (4 ml) and finally 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bromide (0.221 g, 0.00054 mole) dissolved in dry chloroform (2 ml). The mixture was stirred in the dark at room temperature for 6 days, (0.490 g, 0.0019 mole), sodium hydride (0.092 g, 0.00192 mole), tetra-*n*-butylammonium bromide (0.006 g, 0.0000019 mole), iodine (0.002 g) in dry tetrahydrofuran (4 ml) afforded **5b** (0.325 g, 34%); ir (film): 1680, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.40 (1H, *H*-Ar, s), 5.88 (1H, C*H*O), 4.60-4.90 (2H, CH_2O), 3.60-4.40 (6H, C*H*O), 3.95 (3H. CH_3O, s), 3.85 (3H, CH_3O, s), 2.70 (2H, CH_2C=O, s), 1.15-1.70 (18H, CH_3C).

Anal. Calcd. for $C_{26}H_{36}O_{10}$: C, 61.41; H, 7.14. Found: C, 61.14; H, 7.11.

7-Ethoxy-8-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl)methyl-2,2-dimethyl-6-methoxychromene (**6a**).

Sodium borohydride (0.004 g, 0.00013 mole) was added to a stirred solution of **5a** (0.067 g, 0.00013 mole) in methanol (3 ml). The mixture was stirred for 30 minutes at room temperature, neutralized with 2*N* hydrochloric acid and extracted with chloroform (3 × 10 ml). The organic layers were washed with saturated aqueous sodium chloride solution, dried and evaporated to give a mixture (0.052 g) of **6a** and the corresponding chromanol. Filtration through a silica gel column gave **6a** alone (0.035 g, 54%), as a thick colorless oil; ir (chloroform): 1460, 1425 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 6.55 (1H, *H*-Ar, s), 6.25 (1H, C*H*=C, d, J = 10 Hz), 5.85 (1H, C*H*O), 5.55 (1H, C*H*=C, d, J = 10 Hz), 4.50-4.80 (2H, CH_2O), 3.80-4.40 (8H, C*H*O), 3.85 (3H, CH_3O, s), 1.5-1.7 (21H, CH_3C).

Anal. Calcd. for $C_{27}H_{38}O_9$: C, 64.02; H, 7.56. Found: C, 63.90; H, 7.67.

8-(1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl)methyl-2,2-dimethyl-6,7-dimethoxychromene (**6b**).

Application of the same procedure as described above using **5b** and silver oxide (0.228 g, 0.0108 mole) magnesium sulfate (0.766 g), iodine (0.336 g) and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl (0.442 g, 0.00108 mole) were added in four times. The mixture was filtered and the joined filtrates were washed with 0.1*M* sodium bisulfite, dried and evaporated, the residue was purified by thin layer chroamtography (3 plates, 20 × 20 × 0.25 cm eluted with chloroform diethyl ether 1:1) affording **5c** (0.1 g, 31%), as a thick colorless oil; ir (film): 1750, 1680, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.40 (1H, *H*-Ar, s), 4.10-5.40 (9H, C*H*O), 3.88 (3H, CH_3O, s), 3.81 (3H, CH_3O, s), 2.65 (2H, CH_2C=O, s), 1.80-2.20 (12H, CH_3COO), 1.45 (6H, CH_3C, s).

Anal. Calcd. for $C_{28}H_{36}O_{15} \cdot 3H_2O$: C, 51.70; H, 6.40. Found: C, 52.02; H, 5.97.

8-(2',3',4',6'-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2,2-dimethyl-6,7-dimethoxychromene (**6c**).

Sodium borohydride (0.006 g, 0.00017 mole) was added to a stirred solution of **6** (0.100 g, 0.00017 mole) in methanol (3 ml). The mixture was stirred for 30 minutes at room temperature, neutralized with 2*N* hydrochloric acid and extracted with chloroform (3 × 10 ml). The organic layers were washed with saturated aqueous sodium chloride solution, dried and evaporated to give **6c** (0.087 g, 88%) as a thick colorless oil; ir (film): 1750, 1480 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 6.58 (1H, *H*-Ar, s), 6.25 (1H, C*H*=C, d, J = 10 Hz), 5.55 (1H, C*H*=C, d, J = 10 Hz), 4.10-5.25 (9H, C*H*O), 3.85 (6H, CH_3O, s), 1.60-3.20 (12H, CH_3COO), 1.40 (6H, CH_3C, s).

Anal. Calcd. for $C_{28}H_{36}O_{13}$: C, 57.93; H, 6.20. Found: C, 57.88; H, 6.56.

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