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Note

A mild and selective method for cleavage of *O*-acetyl groups with dibutyltin oxide

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Abstract

A mild and efficient neutral method for the cleavage of *O*-acetyl groups with dibutyltin oxide has been developed. This method is especially useful in the synthesis of glycosides containing base- or acid-sensitive multifunctional groups.

Keywords: Dibutyltin oxide; Deacetylation; Acetate; Glycoside

Selective protection and deprotection of functional groups are of importance in organic synthesis.[1] Selective O-deacylation of carbohydrates under mild conditions is not only necessary for the synthesis of some natural glycosides, but is also of great synthetic value, as the products thus prepared may have further synthetic utility as versatile intermediates. Various methods and deacylating reagents have been introduced for this purpose.[2–5] Organotin compounds have been introduced for selective acylation, alkylation and oxidation to prepare intermediates for carbohydrate synthesis.[6–8] We have recently developed a simple and efficient method for the cleavage of *O*-acetyl groups with dibutyltin oxide (Bu_2SnO) in the synthesis of a telomerase inhibitor.[9] Dibutyltin oxide in methanol has been used in the selective O-acylation of ribonucleosides[8] and in microwave-mediated N-acylation of 1,2- and 1,3-amino alcohols.[10] Mascaretti et al. reported that cleavage of carboxylic esters by Bu_2SnO was inefficient compared with other organotin compounds.[11] However, selective deacylation of esters of glycosyl units using Bu_2SnO as the catalyst in the synthesis of glycosides has been little studied from the reverse viewpoint. In this paper, we describe the use of Bu_2SnO as an O-deacetylation reagent in the synthesis of various free-OH glycosides.

At first, phenyl glucosides were selected as substrates. As shown in Table 1, the best results were obtained for a series of phenyl glycosides. The examples quoted in the table show clearly that the selective cleavage of multifunctional molecules is possible. The chemoselective hydrolysis of the acetyl groups in the glycosyl unit with Bu_2SnO was found to be excellent. When the per-*O*-acetylated glycoside was stirred in methanol in the presence of 10 mol% of Bu_2SnO at reflux, the acetyl groups in the phenyl glucosides were smoothly deprotected in very good yield. If the catalyst concentration was increased to 50 mol%, the reaction time would be reduced noticeably from 8 to 2 h (entry 5). Other acyl groups including acetanilide and benzoyl ester of genins were stable under these conditions (entries 2 and 6).

These results prompted us to investigate the applicability and limitations of cleavage of acetate groups with Bu_2SnO in other glycosides. Several diterpene glycosides and steroid glycoside derivatives were used as substrates (Table 2). As expected, the substrates containing acid- or base-sensitive functional groups were smoothly deprotected without decomposition. Nevertheless, the amount of catalyst had to be increased because the C-2′ acetyl group of the glycosyl moiety was difficult to deprotect in spite of longer reaction times (entries 1, 3 and 4). When the amount of catalyst was increased to a ratio of 1:1, the reaction

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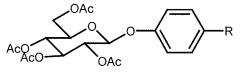
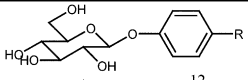
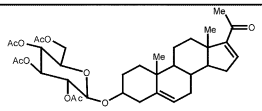
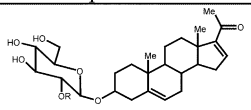
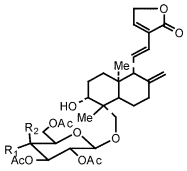
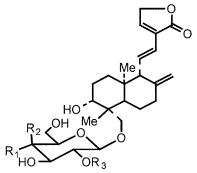
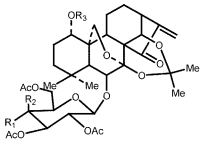
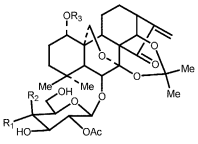
Table 1
Deacetylation of 4-substituted phenyl glucosides[a]

Entry	substrate	time (h)	product	isolated yield (%)
				
1	R = -CHO	8	**1** R = -CHO[12]	90.5
2	R = -NHAc	10	**2** R = -NHAc[13]	82.3
3	R = -$COCH_3$	8	**3** R = -$COCH_3$[14]	90.1
4	R = -NO_2	8	**4** R = -NO_2[15]	91.5
5	R = -NO_2	2[b)]	R = -NO_2	90.3
6	R = -COOEt	8	**5** R = -COOEt[12]	92.3
7	R = -OAc	8	**6** R = -OH[16]	87.7

(a) catalyst:substrate = 1:10. (b) catalyst:substrate = 1:2.

Table 2
Deacetylation of glycosides[a]

Entry	substrate	time (h)	product	isolated yield (%)
				
1		36	**7** R = Ac	27.2[b)]
2		24	**8** R = H	86.8
				
3	R_1 = H, R_2 = OAc	36	**9** R_1 = H, R_2 = OH, R_3 = Ac	28.8[b)]
4	R_1 = OAc, R_2 = H	36	**10** R_1 = OH, R_2 = H, R_3 = Ac	24.4[b)]
5	R_1 = H, R_2 = OAc	30	**11** R_1 = H, R_2 = OH, R_3 = H	87.6
6	R_1 = OAc, R_2 = H	30	**12** R_1 = OH, R_2 = H, R_3 = H	86.5
				
7	R_1 = OAc, R_2 = H, R_3 = Ac	36	**13** R_1 = OH, R_2 = H, R_3 = Ac	83.7
8	R_1 = H, R_2 = OAc, R_3 = Ac	36	**14** R_1 = H, R_2 = OH, R_3 = Ac	88.6
9	R_1 = OAc, R_2 = H, R_3 = H	36	**15** R_1 = OH, R_2 = H, R_3 = H	87.5
10	R_1 = H, R_2 = OAc, R_3 = H	36	**16** R_1 = H, R_2 = OH, R_3 = H	84.2

(a) catalyst:substrate = 1:1. (b) catalyst:substrate = 1:2; the product was isolated from the mixture of R (R_3) = Ac and R (R_3) = H.

became smooth, but the C-2′ acetate derivative was slow to disappear, as determined by TLC monitoring. In entries 7–10, the 2′-*O*-acetyl group was not deprotected after increasing catalyst to ratio 2:1. But the others were completely deprotected under the same reaction conditions. In the ^{1}H NMR spectra, the protons on C-1′ of the products of the entries 7–10 appear at lower field [δ 5.07–5.15] than those of the products of entries 1, 3 and 4 [δ 4.35–4.58]. So different results should be caused by the steric hindrance of the genin units. Furthermore, the acetyl groups in the genins were stable (entries 7 and 8), a result that was similar to that observed in the genins of phenyl glucosides.

In summary, Bu_2SnO is an active catalyst for deacetylation of glycosides under mild conditions, which allows various functional groups to be tolerated and high selectivities between acyl groups of a glycoside and the genin. The acyl groups in the genin were found to be stable compared with the alcoholic acetates in the glycoside. Further studies on the mechanism and applications of the reaction are in progress in our laboratory.

1. Experimental

General methods.—TLC was performed on precoated plates of Silica Gel 60 F_{254}. Components were detected by UV light. Elemental analyses were carried out on a MOD 1106 analyzer. Infrared spectra were recorded on a Shimadzu IR-435 instrument using KBr disks in the 400–4000 cm^{-1} region. Melting points were determined on a WC-1 melting-point apparatus and are uncorrected. NMR spectra were taken with Me_4Si as the internal standard on a Bruker DPX-400 spectrometer, and the chemical shifts are given in δ values. Mass spectra were taken with a Bruker Esquire 3000 mass spectrometer.

General procedure for the synthesis of glycosides.—An amount of glycoside was heated under reflux in dry MeOH containing Bu_2SnO (the indicated mol equiv) for the indicated time (Tables 1 and 2). The product was afforded by flash chromatography using mixtures of $CHCl_3$ and MeOH as eluting solvents.

4-Formylphenyl β-D-glucopyranoside (**1**):[12] mp 155–157 °C; ^{1}H NMR (acetone-d_6): δ 9.92 (s, 1 H, CHO), 7.92, 7.30 (d, each 2 H, *J* 8.8 Hz, ArH), 5.18 (d, 1 H, *J* 7.6 Hz, H-1′), 3.93 (dd, 1 H, *J* 2.0, 12.0 Hz, H-6′), 3.73 (dd, 1 H, *J* 5.6, 12.0 Hz, H-6′), 3.66 (m, 1 H, H-5′), 3.60 (m, 2 H, H-3′, H-2′), 3.49 (t, 1 H, *J* 8.8 Hz, H-4′).

4-(*N*-Acetamido)phenyl D-glucopyranoside (**2**):[13] mp 206–208 °C; ^{1}H NMR (acetone-d_6): δ 9.74 (s, 1 H, NH), 7.51 (m, 2 H, ArH), 7.00 (m, 2 H, ArH), 4.83 (d, 1 H, *J* 7.2 Hz, H-1′), 3.80 (dd, 1 H, *J* 1.6, 12.0 Hz, H-6′), 3.62 (dd, 1 H, *J* 5.2, 12.0 Hz, H-6′), 3.47 (m, 1 H, H-5′), 3.38 (m, 2 H, H-3′, H-2′), 3.30 (t, 1 H, *J* 8.4 Hz, H-4′), 2.03 (s, 3 H, CH_3CO).

4-Acetylphenyl D-glucopyranoside (**3**):[14] mp 192–193 °C; ^{1}H NMR (acetone-d_6): δ 7.92, 7.11 (d, each 2 H, *J* 8.8 Hz, ArH), 5.00 (d, 1 H, *J* 7.2 Hz, H-1′), 3.69 (dd, 1 H, *J* 1.6, 11.6 Hz, H-6′), 3.46 (dd, 1 H, *J* 5.6, 11.6 Hz, H-6′), 3.38 (m, 1 H, H-5′), 3.30 (m, 2 H, H-3′, H-2′), 3.18 (t, 1 H, *J* 8.8 Hz, H-4′), 2.51 (s, 3 H, CH_3CO).

4-Nitrophenyl D-glucopyranoside (**4**):[15] mp 165–167 °C; ^{1}H NMR (acetone-d_6): δ 8.30, 7.39 (m, each 2 H, ArH), 5.28 (d, 1 H, *J* 7.2 Hz, H-1′), 4.01 (dd, 1 H, *J* 1.6, 12.0 Hz, H-6′), 3.81 (dd, 1 H, *J* 5.6, 12.0 Hz, H-6′), 3.74–3.63 (m, 3 H, H-5′, H-3′, H-2′), 3.56 (dd, 1 H, *J* 9.2, 8.8 Hz, H-4′).

4-Ethoxycarbonylphenyl D-glucopyranoside (**5**):[12] mp 214–217 °C; ^{1}H NMR (Me_2SO-d_6): δ 7.90, 7.12 (d, each 2 H, *J* 8.0 Hz, ArH), 4.98 (d, 1 H, *J* 6.8 Hz, H-1′), 4.28 (q, 2 H, *J* 6.8 Hz, OCH_2), 3.69 (d, 1 H, *J* 11.6 Hz, H-6′), 3.47 (dd, 1 H, *J* 5.6, 11.6 Hz, H-6′), 3.39–3.23 (m, 3 H, H-5′, H-3′, H-2′), 3.18 (t, 1 H, *J* 8.8 Hz, H-4′), 1.31 (t, 3 H, *J* 6.8 Hz, CH_3).

4-Hydroxyphenyl D-glucopyranoside (**6**):[16] mp 158–161 °C; ^{1}H NMR (Me_2SO-d_6): δ 6.84 (d, 2 H, *J* 9.2 Hz, ArH), 6.62 (d, 2 H, *J* 8.8 Hz, ArH), 4.62 (d, 1 H, *J* 7.6 Hz, H-1′), 3.68 (d, 1 H, *J* 12.0 Hz, H-6′), 3.45 (dd, 1 H, *J* 5.6, 12.0 Hz, H-6′), 3.45–3.11 (m, 4 H, H-5′, H-3′, H-2′, H-4′).

3-*O*-(2-*O*-Acetyl-β-D-glucopyranosyl)-16-dehydropregnenolone (**7**): mp 158–160 °C; IR (KBr): 1739 (C=O), 1666 cm^{-1} (C=C); ^{1}H NMR (acetone-d_6): δ 6.82 (s, 1 H, H-16), 5.39 (br s, 1 H, H-6), 4.67 (t, 1 H, *J* 8.0 Hz, H-2′), 4.58 (d, 1 H, *J* 8.2 Hz, H-1′), 3.81 (d, 1 H, *J* 10.8 Hz, H-6′), 3.67, 3.30 (m, 5 H, H-6′, H-3′, H-3, H-4′, H-5′), 2.21 (s, 3 H, H_3-21), 2.02 (s, 3 H, CH_3CO), 1.04, 0.90 (s, each 3 H, $CH_3 \times 2$); ESIMS (*m*/*z*): 541 ($[M + Na]^+$), 581 ($[M - CH_3COOH + Na]^+$); Anal. Calcd for $C_{29}H_{42}O_8$ (518.64): C, 67.16; H, 8.16. Found: C, 67.41; H, 7.98.

3-*O*-β-D-Glucopyranosyl-16-dehydropregnenolone (**8**): mp 175–177 °C; IR (KBr): 1739 (C=O), 1666 cm^{-1} (C=C); ^{1}H NMR (acetone-d_6): δ 6.82 (s, 1 H, H-16), 5.38 (br s, 1 H, H-6), 4.40 (d, 1 H, *J* 7.6 Hz, H-1′), 3.80 (d, 1 H, *J* 10.8 Hz, H-6′), 3.60 (m, 3 H, H-6′, H-3′, H-3), 3.35 (m, 2 H, H-4′, H-5′), 3.12 (t, 1 H, *J* 7.3 Hz, H-2′), 2.21 (s, 3 H, H_3-21), 1.05, 0.90 (s, each 3 H, $CH_3 \times 2$); ESIMS (*m*/*z*): 499 ($[M + Na]^+$), 484 ($[M + H_2O]^+$); Anal. Calcd for $C_{27}H_{40}O_7$ (476.60): C, 68.04; H, 8.46. Found: C, 68.33; H, 8.35.

19-*O*-(2′-*O*-Acetyl-β-D-galactopyranosyl)-14-deoxy-11,12-didehydroandrographiside (**9**): mp 128–129 °C; IR (KBr): 1752 (C=O), 1644 (C=C), 892 cm^{-1} (=C-H); ^{1}H NMR (acetone-d_6): δ 7.41 (s, 1 H, H-14), 6.77 (dd, 1 H, *J* 10.0, 15.6 Hz, H-11), 6.20 (d, 1 H, *J* 16.0 Hz, H-12), 4.85 (dd, 1 H, *J* 8.0, 10.0 Hz, H-2′), 4.75 (s, 2 H, H_2-15), 4.63, 4.37 (d, each 1 H, *J* 1.6 Hz, H_2-17), 4.35 (d, 1 H, *J* 8.0 Hz, H-1′), 3.84 (d, 1 H, *J* 3.2 Hz, H-4′), 3.79 (t, 1 H, *J* 3.2 Hz, H-6′), 3.77 (t, 1 H, *J* 3.2 Hz, H-6′), 3.67 (m, 1 H, H-3′), 3.62 (m, 1 H, H-5′), 3.44, 3.04 (d, 1 H, *J* 11.2 Hz, H-19), 3.39 (dd, 1 H, *J* 4.0, 11.6 Hz, H-3), 1.91 (s, 3 H, CH_3CO), 1.22, 0.67 (s, each 3 H, $CH_3 \times 2$); ESIMS (*m*/*z*): 559 ($[M + Na]^+$), 537 ($[M + H]^+$); Anal. Calcd for $C_{28}H_{40}O_{10}$ (536.61): C, 62.67; H, 7.51. Found: C, 62.56; H, 7.59.

19-*O*-(2′-*O*-Acetyl-β-D-glucopyranosyl)-14-deoxy-11,12-didehydroandrographiside (**10**): mp 124–126 °C; IR (KBr): 1752 (C=O), 1645 (C=C), 893 cm^{-1} (=C-H); ^{1}H NMR (acetone-d_6): δ 7.53 (s, 1 H, H-14), 6.89 (1 H, dd, *J* 10.0, 16.0 Hz, H-11), 6.19 (d, 1 H, *J* 16.0 Hz, H-12), 4.87 (s, 2 H, H_2-15), 4.76, 4.50 (d, each 1 H, *J* 1.2 Hz, H_2-17), 4.65 (dd, 1 H, *J* 9.6, 8.8 Hz, H-2′), 4.54 (d, 1 H, *J* 8.0 Hz, H-1′), 3.90, 3.18 (d, each 1 H, *J* 11.2 Hz, H_2-19), 3.84 (d, 1 H, *J* 11.8 Hz, H-6′), 3.70 (dd, 1 H, *J* 11.8, 5.6 Hz, H-6′), 3.61 (t, 1 H, *J* 8.0 Hz, H-3′), 3.54 (m, 1 H, H-3), 3.46 (t, 1 H, *J* 8.8 Hz, H-4′), 3.35 (m, 1 H, H-5′), 1.15, 0.80 (s, each 3 H, $CH_3 \times 2$); ESIMS (*m*/*z*): 559 ($[M + Na]^+$), 499 ($[M - CH_3COOH + Na]^+$); Anal. Calcd for $C_{28}H_{40}O_{10}$ (536.61): C, 62.67; H, 7.51. Found: C, 62.86; H, 7.74.

19-*O*-β-D-Galactopyranosyl-14-deoxy-11,12-didehydroandrographiside (**11**): mp 132–134 °C; IR (KBr):

1751 (C=O), 1644 (C=C), 891 cm^{-1} (=C-H); ^1H NMR (acetone-d_6): δ 7.52 (s, 1 H, H-14), 6.90 (dd, 1 H, *J* 10.0, 16.0 Hz, H-11), 6.18 (d, 1 H, *J* 16.0 Hz, H-12), 4.86 (s, 2 H, H_2-15), 4.75, 4.49 (s, each 1 H, H_2-17), 4.29 (d, 1 H, *J* 6.4 Hz, H-1′), 3.96, 3.21 (d, each 1 H, *J* 10.8 Hz, H_2-19), 3.87 (m, 1 H, H-3′), 3.75 (d, 1 H, *J* 4.0 Hz, H-4′), 3.71 (m, 2 H, H-6′), 3.56 (dd, 1 H, *J* 3.6, 11.6 Hz, H-3), 3.51 (d, 1 H, *J* 4.0 Hz, H-5′), 3.48 (m, 1 H, H-2′), 1.22, 0.83 (s, each 3 H, $CH_3 \times 2$); ESIMS (*m*/*z*): 517 ($[M + Na]^+$); Anal. Calcd for $C_{26}H_{38}O_9$ (494.57): C, 63.14; H, 7.44. Found: C, 26.95; H, 7.26.

19-*O*-β-D-Glucopyranosyl-14-deoxy-11,12-didehydroandrographiside (**12**): mp 138–140 °C; IR (KBr): 1751 (C=O), 1644 (C=C), 893 cm^{-1} (=C-H); ^1H NMR (acetone-d_6): δ 7.53 (s, 1 H, H-14), 6.95 (dd, 1 H, *J* 10.0, 15.6 Hz, H-11), 6.18 (d, 1 H, *J* 15.8 Hz, H-12), 4.87 (d, 2 H, *J* 1.6 Hz, H_2-15), 4.76, 4.51 (d, 1 H, *J* 1.6 Hz, H_2-17), 4.38 (d, 1 H, *J* 7.6 Hz, H-1′), 4.26 (m, 1 H, H-4′), 3.96, 3.23 (d, 1 H, *J* 11.2 Hz, H-19), 3.81 (dd, 1 H, *J* 2.4, 11.6 Hz, H-6′), 3.66 (dd, 1 H, *J* 5.6, 11.6 Hz, H-6′), 3.59 (dd, 1 H, *J* 4.0, 12.0 Hz, H-3), 3.37 (t, 1 H, *J* 2.0 Hz, H-3′), 3.31 (m, 1 H, H-5′), 3.14 (t, 1 H, *J* 2.0 Hz, H-2′), 1.22, 0.83 (s, each 3 H, $CH_3 \times 2$); ESIMS (*m*/*z*): 517 ($[M + Na]^+$), 495 ($[M + H]^+$); Anal. Calcd for $C_{26}H_{38}O_9$ (494.57): C, 63.14; H, 7.44. Found: C, 63.01; H, 7.40.

1-*O*-Acetyl-6-(2-*O*-acetyl-β-D-glucopyranosyl)-7:14-*O*-isopropylideneoridonin (**13**): mp 286–288 °C; IR (KBr): 1743, 1728 (C=O), 1651 (C=C), 912 cm^{-1} (=C-H); ^1H NMR (acetone-d_6): δ 5.82, 5.34 (s, each 1 H, H_2-17), 5.14 (d, 1 H, *J* 8.4 Hz, H-1′), 4.86 (s, 1 H, H-14), 4.78 (m, 1 H, H-2′), 4.60 (dd, 1 H, *J* 5.6, 10.0 Hz, H-1), 4.35 (d, 1 H, *J* 9.2 Hz, H-6), 4.29, 4.09 (d, each 1 H, *J* 10.0 Hz, H_2-20), 3.93 (dd, 1 H, *J* 2.4, 11.2 Hz, H-6′), 3.72 (dd, 1 H, *J* 11.2, 5.6 Hz, H-6′), 3.45–3.39 (m, 2 H, H-3′, H-5′), 3.30 (m, 1 H, H-4′), 2.94 (d, 1 H, *J* 10.0 Hz, H-13), 2.47 (dt, 1 H, *J* 8.4, 14.0 Hz, H-12), 1.94, 1.92 (s, each 3 H, $CH_3CO \times 2$), 1.88 (m, 1 H, H-11), 1.76 (dd, 1 H, *J* 5.2, 12.4 Hz, H-9), 1.67 (d, 1 H, *J* 9.2 Hz, H-5), 1.64–1.48 (m, 2 H, H-2, H-12), 1.46–1.12 (m, 4 H, H-2, H_2-3, H-11), 1.61, 1.32, 1.24, 1.18 (s, each 3 H, $CH_3 \times 4$); ESIMS (*m*/*z*): 673 ($[M + Na]^+$), 613 ($[M - CH_3COOH + Na]^+$), 451 ($[M - \{Glc\text{-}OAc\} + Na]^+$). Anal. Calcd for $C_{33}H_{46}O_{13}$ (650.71): C, 60.91; H, 7.13. Found: C, 60.70; H, 7.32.

1-*O*-Acetyl-6-(2′-*O*-acetyl-β-D-galactopyranosyl)-7:14-*O*-isopropylideneoridonin (**14**): mp 277–279 °C; IR (KBr): 1742 (C=O), 1651 (C=C), 909 cm^{-1} (=C-H); ^1H NMR (acetone-d_6): δ 5.82, 5.33 (s, each 1 H, H_2-17), 5.10–5.03 (m, 2 H, H-1′, H-2′), 4.86 (d, 1 H, *J* 1.6 Hz, H-14), 4.60 (dd, 1 H, *J* 5.6, 10.4 Hz, H-1), 4.34 (d, 1 H, *J* 9.2 Hz, H-6), 4.28, 4.09 (d, each 1 H, *J* 9.2 Hz, H_2-20), 3.94 (m, 1 H, H-4′), 3.88–3.77 (m, 2 H, H-6′), 3.57–3.49 (m, 2 H, H-3′, H-5′), 2.94 (d, 1 H, *J* 8.0 Hz, H-13), 2.46 (dt, 1 H, *J* 8.8, 14.0 Hz, H-12), 1.94, 1.92 (s, each 3 H, $CH_3CO \times 2$), 1.60, 1.31 (s, each 3 H, $CH_3 \times 2$), 1.22, 1.19 (s, each 3 H, $CH_3 \times 2$); ESIMS (*m*/*z*): 673 ($[M + Na]^+$), 668 ($[M + H_2O]^+$); Anal. Calcd for $C_{33}H_{46}O_{13}$ (650.71): C, 60.91; H, 7.13. Found: C, 60.81; H, 7.34.

6-(2′-*O*-acetyl-β-D-glucopyranosyl)-7:14-*O*-isopropylideneoridonin (**15**): mp 154–156 °C; IR (KBr): 1738, 1712 (C=O), 1647 (C=C), 908 cm^{-1} (=C-H); ^1H NMR (acetone-d_6): δ 5.81, 5.32 (s, each 1 H, H_2-17), 5.15 (d, 1 H, *J* 8.0 Hz, H-1′), 4.87 (d, 1 H, *J* 1.2 Hz, H-14), 4.78 (m, 1 H, H-2′), 4.30 (m, 2 H, H-6, H-20), 3.95 (m, 2 H, H-20, H-6′), 3.71 (m, 1 H, H-6′), 3.44 (m, 3 H, H-3′, H-3, H-5′), 3.30 (m, 1 H, H-4′), 2.94 (br s, 1 H, H-13), 1.92 (s, 3 H, CH_3CO), 1.60, 1.32, 1.21, 1.15 (s, each 3 H, $CH_3 \times 4$); ESIMS (*m*/*z*): 631 ($[M + Na]^+$), 571 ($[M - CH_3COOH + Na]^+$); Anal. Calcd for $C_{31}H_{44}O_{12}$ (608.67): C, 61.17; H, 7.29. Found: C, 60.89; H, 7.11.

6-*O*-(2′-*O*-Acetyl-β-D-galactopyranosyl)-7:14-*O*-isopropylideneoridonin (**16**): mp 178–180 °C; IR (KBr): 1740, 1711 (C=O), 1647 (C=C), 907 cm^{-1} (=C-H); ^1H NMR (acetone-d_6): δ 5.81, 5.32 (s, each 1 H, H_2-17), 5.06 (m, 2 H, H-1′, H-2′), 4.85 (d, 1 H, *J* 1.6 Hz, H-14), 4.30 (d, 1 H, *J* 9.2 Hz, H-6), 4.26, 3.96 (d, each 1 H, *J* 10.0 Hz, H_2-20), 3.93 (d, 1 H, *J* 2.8 Hz, H-4′), 3.84 (dd, 1 H, *J* 6.4, 10.8 Hz, H-6′), 3.77 (dd, 1 H, *J* 10.8, 5.6 Hz, H-6′), 3.51 (m, 2 H, H-3′, H-5′), 3.43 (dd, 1 H, *J* 5.6, 11.2 Hz, H-1), 2.93 (d, 1 H, *J* 9.2 Hz, H-13), 2.47 (dt, 1 H, *J* 10.8, 13.6 Hz, H-12), 1.92 (s, 3 H, CH_3CO), 1.59, 1.31, 1.18, 1.16 (s, each 3 H, $CH_3 \times 4$); ESIMS (*m*/*z*): 631 ($[M + Na]^+$), 571 ($[M - CH_3COOH + Na]^+$); Anal. Calcd for $C_{31}H_{44}O_{12}$ (608.67): C, 61.17; H, 7.29. Found: C, 61.40; H, 7.12.

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