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CARBOHYDRATE
RESEARCH

Note

Synthesis of 6-*O*-acetyl-2,3,4-tri-*O*-[(*S*)-2-methylbutyryl]sucrose and the three regioisomers of 6-*O*-acetyl-2,3,4-*O*-[(*S*)-2-methylbutyryl]-di-*O*-[(*S*)-3-methylpentanoyl]sucrose, naturally occurring fatty acid esters of sucrose found in tobacco [1]

Stefan Oscarson *, Helena Ritzén

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

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Fatty acid esters of sucrose are found on the surface of leaves of tobacco, and function as flavour precursors and also as insecticides and bactericides [1–4]. Structural investigations of isolated sucrose esters have shown that these are usually acylated only in the glucose moiety, that they have a 6-*O*-acetyl group, and that the 2-, 3-, and 4-positions are esterified with various fatty acids [1,2]. Sucrose esters with other substitutional patterns have also been found [4].

In an earlier publication we described the synthesis of a precursor, 6-*O*-acetyl-3-*O*-allyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)sucrose [5] (**1**), from which it should be possible to synthesise all the different permutations of fatty acid esters esterified to the 2-, 3-, and 4-positions of the glucose moiety. We also described the synthesis from the precursor of the major component extracted from Oriental tobacco, i.e., 6-*O*-acetyl-2,3,4-tri-*O*-[(*S*)-3-methylpentanoyl]sucrose [5]. We now describe the synthesis of 6-*O*-

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* Corresponding author.

[1] Partially esterified sucrose derivatives, Part III. For Parts I and II, see refs. [5,6].

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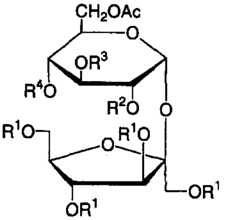
acetyl-2,3,4-tri-*O*-[(*S*)-2-methylbutyryl]sucrose (**4**) and also of the three possible regioisomers esterified with two molecules of (*S*)-3-methylpentanoic acid (a C_6 fatty acid) and one of (*S*)-2-methylbutyric acid (C_5) in the 2-, 3-, and 4-positions (**9**, **13**, and **18**). These derivatives will be used to assign the substitution pattern found in the natural products, to find better separation systems for the natural products, and also to function as model substances to find out if and how the substitution pattern can be determined by spectroscopic methods (NMR and MS).



1 R^1= Bn, R^2= *p*MBn, R^3= All, R^4=H
2 R^1= Bn, R^2= R^3= R^4= H
3 R^1= Bn, R^2= R^3= R^4= COCH(Me)CH_2Me
4 R^1= H, R^2= R^3= R^4= COCH(Me)CH_2Me
5 R^1= Bn, R^2= *p*MBn, R^3= All, R^4= COCH(Me)CH_2Me
6 R^1= Bn, R^2= *p*MBn, R^3= H, R^4= COCH(Me)CH_2Me
7 R^1= Bn, R^2= R^3=H, R^4= COCH(Me)CH_2Me
8 R^1= Bn, R^2= R^3= $COCH_2$CH(Me)CH_2Me, R^4= COCH(Me)CH_2Me
9 R^1= H, R^2= R^3= $COCH_2$CH(Me)CH_2Me, R^4= COCH(Me)CH_2Me
10 R^1= Bn, R^2= *p*MBn, R^3= R^4= $COCH_2$CH(Me)CH_2Me
11 R^1= Bn, R^2= H, R^3= R^4= $COCH_2$CH(Me)CH_2Me
12 R^1= Bn, R^2= COCH(Me)CH_2Me, R^3= R^4= $COCH_2$CH(Me)CH_2Me
13 R^1= H, R^2= COCH(Me)CH_2Me, R^3= R^4= $COCH_2$CH(Me)CH_2Me
14 R^1= Bn, R^2= R^4= H, R^3= All
15 R^1= Bn, R^2= R^4= $COCH_2$CH(Me)CH_2Me, R^3= All
16 R^1= Bn, R^2= R^4= $COCH_2$CH(Me)CH_2Me, R^3= H
17 R^1= Bn, R^2= R^4= $COCH_2$CH(Me)CH_2Me, R^3= COCH(Me)CH_2Me
18 R^1= H, R^2= R^4= $COCH_2$CH(Me)CH_2Me, R^3= COCH(Me)CH_2Me

All = allyl *p*MBn = *p*-methoxybenzyl

The present syntheses parallel those in the earlier publication. They start from the precursor **1** and the protecting groups are removed in the same way, the 4-methoxybenzyl group by treatment with cerium(IV) ammonium nitrate in acetonitrile–water, the allyl group by isomerisation using tris(triphenylphosphine)rhodium(I) chloride followed by hydrolysis of the vinyl ether with mercury(II) bromide, and the benzyl ethers by hydrogenolysis over palladium on charcoal. The esterifications, however, are accomplished using the carboxylic acid and dicyclohexylcarbodiimide (DCC) instead of the acid chloride and pyridine used earlier, since the latter method in some of the present attempted esterifications gave a non-acylated derivative as main product. The reaction

Table 1
^{13}C NMR shifts of the fatty acid carbonyl carbons in the sucrose esters

Substance	2,3,4-tri-C_6 [5]	2,3,4-tri-C_5 (**4**)	2,3-di-C_6-4-C_5 (**9**)	3,4-di-C_6-2-C_5 (**13**)	2,4-di-C_6-3-C_5 (**18**)
C_5-acid carbonyl signals		176.8		176.8	
		176.1			175.9
		175.2	175.2		
C_6-acid carbonyl signals	173.0		173.0		173.0
	172.7		172.6	172.5	
	171.8			171.8	171.8

steps, without optimisation, normally proceeded in good yields (70–90%). The only problem encountered sometimes was a low yield in the debenzylation steps.

Esterification of 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzylsucrose [5] (**2**) with 2-(*S*)-methylbutyric acid gave the tetraacyl derivative **3** (96%), which was deprotected to give the first target compound **4** (91%).

Esterification of **1** with 2-(*S*)-methylbutyric acid to give **5** (96%) was followed by removal of the allyl group (→ **6**, 78%) and the 4-methoxybenzyl group to yield the 2,3-diol **7** (74%), which was acylated with 3-(*S*)-methylpentanoic acid (→ **8**, 93%) and then debenzylated to give the 4-*O*-C_5 target isomer **9** (68%).

Removal of the allyl group from the precursor **1** gave, as described earlier, 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)sucrose [5], which was esterified to give the 3,4-di-*O*-(*S*)-3-methylpentanoyl derivative **10** (69%). The 4-methoxybenzyl group was removed (→ **11**, 73%), whereafter acylation with 2-(*S*)-methylbutyric acid (→ **12**, 88%) and catalytic hydrogenolysis gave the 2-*O*-C_5 target derivative **13** (28%).

Removal of the 4-methoxybenzyl group from **1** gave the 2,4-diol **14** (65%), which was esterified with 3-(*S*)-methylpentanoic acid to yield **15** (67%). Deallylation (→ **16**, 71%) followed by esterification with 2-(*S*)-methylbutyric acid afforded the tetraacyl derivative **17** (78%), which after catalytic hydrogenolysis gave the 3-*O*-C_5 target compound **18** (77%).

Examination of the ^{13}C NMR carbonyl signals of the fatty acids in the tetraacylated target compounds (see Table 1) strongly indicates that these signals could be used for identifying the substitution pattern of these and similar compounds.

1. Experimental

General methods.—These were as previously described [7]. The purity and homogeneity of all the target products were established by TLC (9:1 chloroform–MeOH) and by ^{1}H and ^{13}C NMR spectroscopy.

6-O-Acetyl-2,3,4-tri-O-[(S)-2-methylbutyryl]sucrose (**4**).—Dicyclohexylcarbodiimide (DCC) (315 mg) was added to a solution of 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzylsucrose [5] (**2**; 234 mg), 2-(*S*)-methylbutyric acid (170 μL), and 4-methylaminopyridine (catalytic amount) in CCl_4 (10 mL). The mixture was stirred overnight at room temperature, then filtered, and concentrated. Silica gel column chromatography (9:1 toluene–EtOAc) of the residue gave 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-2,3,4-tri-*O*-[(*S*)-2-methylbutyryl]sucrose (**3**; 300 mg, 96%); ^{13}C NMR data (CDCl$_3$): δ 11.4, 2 × 11.6, 16.0, 16.2, 16.3, 20.7, 2 × 26.3, 26.3, 2 × 40.7, 40.8, 61.5, 67.6, 67.7, 69.8, 70.0, 70.3, 71.8, 72.7, 73.3, 2 × 73.5, 79.3, 80.8, 83.5, 88.5, 104.3, 127.5–128.4, 137.7–138.1, 170.5, 175.0, 175.3, 175.5.

A solution of **3** (300 mg) in aq EtOAc (5 mL) was hydrogenolysed over Pd–C (10%, 50 mg) at 400 kPa for 16 h, then filtered, and concentrated. Column chromatography on silica gel (14:1 CHCl$_3$–MeOH) of the residue yielded **4** (176 mg, 91%), $[\alpha]_D$ +71° (*c* 1.5, CHCl$_3$); NMR data (CDCl$_3$): ^{1}H, δ 4.85 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.2 Hz, H-2), 5.14 (t, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.54 (t, 1 H, H-3), 5.75 (d, 1 H, H-1); ^{13}C, δ 2 × 11.5. 11.6 (*Me*CH$_2$), 16.0, 16.1, 16.2 (*Me*CH), 20.7 (*Me*CO), 26.2, 26.3, 26.4 (Me*C*H$_2$), 40.6, 40.7, 40.8 (Me*C*H), 61.0, 61.8 (C-6,6′), 64.1, 67.7, 68.6, 69.2, 70.9, 73.7, 77.6, 81.7 (C-2–5,1′,3′–5′), 89.0 (C-1), 104.8 (C-2′), 171.0, 175.2, 175.9, 176.8 (C=O).

6-O-Acetyl-4-O-[(S)-2-methylbutyryl]-2,3-di-O-[(S)-3-methylpentanoyl]sucrose (**9**). —Derivative **1** [5] (116 mg) was acylated with (*S*)-2-methylbutyric acid (20 μL), as described above for **2**, to yield, after silica gel chromatography (9:1 toluene–EtOAc), 6-*O*-acetyl-3-*O*-allyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**5**; 122 mg, 96%); ^{13}C NMR data (CDCl$_3$): δ 11.7, 16.5, 20.8, 26.6, 41.2, 55.2, 62.1, 67.9, 68.8, 70.6, 71.5, 71.8, 72.6, 73.1, 73.2, 73.4, 73.8, 78.7, 78.9, 79.4, 81.5, 83.9, 89.5, 104.5, 113.6, 116.3, 127.4–130.1, 134.9, 137.9, 138.0, 160.1, 170.7, 175.2.

A solution of **5** (122 mg) and tris(triphenylphosphine)rhodium(I) chloride (75 mg) in 6:3:1 toluene–EtOH–H$_2$O (7 mL) was boiled under reflux for 24 h, then cooled to room temperature. Mercury(II) bromide (100 mg) was added, and the mixture was stirred for 16 h, then filtered through silica gel, and concentrated. Silica gel column chromatography (9:1 toluene–EtOAc) of the residue gave 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**6**; 93 mg, 78%); ^{13}C NMR data (CDCl$_3$): δ 11.5, 16.6, 20.8, 26.6, 41.3, 55.2, 62.0, 67.6, 69.5, 70.2, 71.1, 71.3, 71.7, 72.7, 73.2, 73.3, 73.6, 78.3, 79.3, 81.0, 83.9, 88.7, 104.4, 113.8, 127.5–130.9, 137.9–138.1, 159.3, 170.6, 175.8.

Cerium(IV) ammonium nitrate (75 mg) was added to a solution of **6** (62 mg) in 9:1 CH$_3$CN–H$_2$O (3 mL). The mixture was stirred for 90 min, then diluted with CH$_2$Cl$_2$, washed with NaHCO$_3$ (aq) and water, dried (Na$_2$SO$_4$), filtered, and concentrated. Silica gel column chromatography (3:1 toluene–EtOAc) of the residue gave 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**7**; 40 mg, 74%); ^{13}C NMR data (CDCl$_3$): δ 11.5, 16.6, 20.8, 26.5, 41.2, 62.0, 68.4, 69.4, 69.7, 71.5, 72.3, 72.7, 73.1, 2 × 73.2, 73.6, 79.9, 82.7, 85.2, 92.1, 104.7, 127.7–128.5, 136.8–137.7, 170.6, 176.0.

Acylation of **7** (35 mg) with (*S*)-3-methylpentanoic acid (15 μL), as described above for **2**, yielded, after silica gel chromatography (19:1 toluene–EtOAc), 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-4-*O*-[(*S*)-2-methylbutyryl]-2,3-di-*O*-[(*S*)-3-methylpentanoyl]sucrose (**8**; 40 mg, 93%); ^{13}C NMR data (CDCl$_3$): δ 11.2, 11.3, 11.5, 19.1, 19.2, 20.8, 26.3, 2 × 29.2, 29.2, 31.5, 31.5, 40.9, 2 × 41.1, 61.6, 67.7, 67.8, 69.7, 70.2, 70.3, 71.6, 72.7, 73.3, 73.3, 73.5, 79.3, 81.3, 83.7, 88.8, 104.5, 127.6–128.4, 137.7–138.1, 170.6, 172.1, 172.2, 175.1.

Compound **8** (37 mg) was debenzylated, as described above for **3**, to give **9** (16 mg, 68%); $[\alpha]_D$ +60° (*c* 0.8, CHCl$_3$); NMR data (CDCl$_3$): ^{1}H, δ 4.92 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.3 Hz, H-2), 5.13 (t, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.55 (t, 1 H, H-3), 5.71 (d, 1 H, H-1); ^{13}C, δ 2 × 11.2, 11.5 (*Me*CH$_2$), 16.2 [MeCH$_2$(*Me*)CHCO], 19.2, 19.2 [MeCH$_2$(*Me*)CHCH$_2$], 20.7 (*Me*CO), 26.3 [Me*C*H$_2$(Me)CHCO], 29.1, 29.2 [Me*C*H$_2$(Me)CHCH$_2$], 31.4, 31.5 [MeCH$_2$(Me)*C*HCH$_2$], 40.8, 40.9, 41.0 (*C*HCO, *C*H$_2$CO), 60.7, 61.7 (C-6,6′), 64.5, 67.7, 68.8, 69.2, 70.6, 73.7, 78.3, 82.0 (C-2–5,1′,3′–5′), 89.2 (C-1), 104.8 (C-2′), 170.9, 172.6, 173.0, 175.2 (C = O). FABMS: *m/z* 687.4 [M + Na]$^+$.

6-O-Acetyl-2-O-[(S)-2-methylbutyryl]-3,4-di-O-[(S)-3-methylpentanoyl]sucrose (**13**). —6-*O*-Acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)sucrose [5] (130 mg) was acylated with (*S*)-3-methylpentanoic acid (60 μL), as described above for **2**, to yield, after silica gel chromatography (19:1 toluene–EtOAc), 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)-3,4-di-*O*-[(*S*)-3-methylpentanoyl]sucrose (**10**; 160 mg, 69%); ^{13}C NMR data (CDCl$_3$): δ 2 × 11.2, 19.1, 19.2. 20.7, 2 × 29.2, 2 × 31.5, 41.1, 41.4, 55.1, 61.9, 67.6, 68.0, 70.4, 71.1, 71.4, 71.6, 72.6, 73.1, 73.4, 73.5, 76.0, 79.4, 81.0, 83.9, 88.9, 104.5, 113.6, 127.5–129.8, 137.8–138.1, 159.1, 170.5, 171.9, 172.2.

The 4-methoxybenzyl group was removed from **10** (110 mg) as described above for **6**, to give, after silica gel chromatography (19:1 toluene–EtOAc, 19:1), 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-3,4-di-*O*-[(*S*)-3-methylpentanoyl]sucrose (**11**; 71 mg, 73%); ^{13}C NMR data (CDCl$_3$): δ 11.2, 11.3, 2 × 19.1, 20.7, 29.2, 29.3, 31.6, 31.9, 41.1, 41.4, 61.8, 67.2, 68.3, 69.6, 71.0, 71.5, 72.4, 73.1, 2 × 73.2, 73.5, 80.0, 82.4, 84.8, 92.0, 104.7, 127.7–128.5, 136.9–137.9, 170.6, 171.8, 173.1.

Compound **11** (71 mg) was acylated with (*S*)-2-methylbutyric acid (15 μL), as described above for **2**, to yield, after silica gel chromatography (19:1 toluene–EtOAc), 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-[(*S*)-2-methylbutyryl]-3,4-di-*O*-[(*S*)-3-methylpentanoyl]sucrose (**12**; 68 mg, 88%); ^{13}C NMR data (CDCl$_3$): δ 2 × 11.2, 11.5, 16.2, 19.1, 19.2, 20.7, 26.4, 29.2, 29.3, 31.3, 31.4, 40.7, 2 × 41.1, 61.6, 67.7, 67.9, 69.8, 70.2, 70.3, 71.6, 72.6, 73.3, 73.3, 73.5, 79.4, 81.1, 83.5, 88.7, 104.4, 127.5–128.4, 137.7–138.1, 170.5, 171.7, 172.1, 175.4.

Derivative **12** (61 mg) was debenzylated as described above for **3**, to give **13** (11 mg, 28%); $[\alpha]_D$ +63° (*c* 0.3, CHCl$_3$); NMR data (CDCl$_3$): ^{1}H, δ 4.84 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.3 Hz, H-2), 5.11 (t, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.55 (t, 1 H, H-3), 5.74 (d, 1 H, H-1); ^{13}C, δ 2 × 11.2, 11.4 (*Me*CH$_2$), 15.9 [CH$_3$CH$_2$(*Me*)CHCO], 19.2, 19.2 [MeCH$_2$(*Me*)CHCH$_2$], 20.7 (*Me*CO), 26.6 [Me*C*H$_2$(Me)CHCO], 29.2, 29.3 [Me*C*H$_2$(Me)CHCH$_2$], 31.4, 31.5 [MeCH$_2$(Me)*C*HCH$_2$], 40.6, 41.0, 41.1 (*C*HCO, *C*H$_2$CO), 60.8, 61.9 (C-6,6′), 64.5, 67.9, 68.7, 69.2, 70.8, 73.7, 78.1, 81.8 (C-2–5,1′,3′–5′), 89.1 (C-1), 104.9 (C-2′), 170.9, 171.8, 172.5, 176.8 (C=O). FABMS: *m/z* 665.4 [M + H]$^+$.

6-O-Acetyl-3-O-[(S)-2-methylbutyryl]-2,4-di-O-[(S)-3-methylpentanoyl]sucrose (**18**). —The 4-methoxybenzyl group was removed from **1** (165 mg) as described above for **6**, to give 6-*O*-acetyl-3-*O*-allyl-1′,3′,4′,6′-tetra-*O*-benzylsucrose (**14**; 93 mg, 65%); ^{13}C NMR data (CDCl$_3$): δ 20.8, 63.2, 69.1, 70.0, 70.4, 71.4, 72.3, 72.6, 72.9, 73.2, 73.6, 73.8, 79.9, 81.8, 83.0, 85.3, 92.8, 104.5, 117.3, 127.7–128.5, 135.2, 136.9–137.8, 171.4.

Acylation of **14** (93 mg) with (*S*)-3-methylpentanoic acid (50 μL), as described above for **2**, gave, after silica gel chromatography (19:1 toluene–EtOAc), 6-*O*-acetyl-3-*O*-allyl-1′,3′,4′,6′-tetra-*O*-benzyl-2,4-di-*O*-[(*S*)-3-methylpentanoyl]sucrose (**15**; 76 mg, 67%), ^{13}C NMR data ($CDCl_3$): δ 2 × 11.2, 2 × 19.2, 20.8, 2 × 29.3, 31.6, 31.7, 41.4, 41.5, 62.0, 68.1, 69.0, 70.6, 71.1, 72.2, 72.6, 73.0, 73.1, 73.3, 73.6, 76.7, 79.5, 82.1, 83.8, 89.5, 104.6, 116.5, 127.6–128.4, 134.5, 137.7–138.1, 170.7, 171.6, 172.0.

Compound **15** (76 mg) was deallylated as described above for **5**, to yield, after silica gel chromatography (9:1 toluene–EtOAc), 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-2,4-di-*O*-[(*S*)-3-methylpentanoyl]sucrose (**16**; 52 mg, 71%); ^{13}C NMR data ($CDCl_3$): δ 11.3, 11.3, 2 × 19.1, 20.8, 29.2, 29.3, 2 × 31.8, 41.2, 41.3, 61.9, 67.7, 70.3, 2 × 70.4, 71.2, 72.6, 72.7, 73.0, 73.2, 73.5, 79.4, 81.7, 83.7, 89.3, 104.4, 127.6–129.0, 137.6–138.0, 170.6, 172.8, 173.1.

Compound **16** (52 mg) was acylated with (*S*)-2-methylbutyric acid (10 μL), as described above for **2**, to yield, after silica gel chromatography (19:1 toluene–EtOAc), 6-*O*-acetyl-1′,3′,4′,6′-tetra-*O*-benzyl-3-*O*-[(*S*)-2-methylbutyryl]-2,4-di-*O*-[(*S*)-3-methylpentanoyl]sucrose (**17**; 44 mg, 78%); ^{13}C NMR data ($CDCl_3$): δ 11.2, 11.2, 11.6, 16.2, 19.1, 19.2, 20.8, 26.5, 29.2, 29.3, 31.4, 31.4, 40.9, 2 × 41.0, 61.7, 67.7, 67.9, 69.8, 70.2, 70.3, 71.6, 72.7, 73.3, 73.3, 73.6, 79.4, 81.4, 83.7, 88.9, 104.5, 127.6–128.4, 137.7–138.1, 170.6, 171.7, 172.1, 175.6.

Compound **17** (39 mg) was debenzylated as described above for **3**, to give **18** (20 mg, 77%); $[\alpha]_D$ +68° (*c* 0.8, $CHCl_3$); NMR data ($CDCl_3$): ^{1}H, δ 4.94 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.3 Hz, H-2), 5.14 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.9 Hz, H-4), 5.53 (t, 1 H, H-3), 5.70 (d, 1 H, H-1); ^{13}C, 2 × 11.2, 11.6 (*Me*CH_2), 16.2 [MeCH_2(*Me*)CHCO], 2 × 19.2 [MeCH_2(*Me*)CHCH_2], 20.7 (*Me*CO), 26.4 [Me*C*H_2(Me)CHCO], 29.1, 29.2 [Me*C*H_2(Me)CHCH_2], 31.3, 31.5 [MeCH_2(Me)*C*HCH_2], 40.8, 40.9, 40.9 (*C*HCO, *C*H_2CO), 60.6, 61.6 (C-6,6′), 64.7, 67.7, 68.8, 69.3, 70.5, 73.6, 78.6, 82.1 (C-2–5,1′,3′–5′), 89.2 (C-1), 104.7 (C-2′), 170.8, 171.8, 173.0, 176.1 (C=O). FABMS: *m/z* 687.3 $[M + Na]^+$.

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