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A SIMPLE SYNTHESIS OF GLUCOSYL GLYCEROLS

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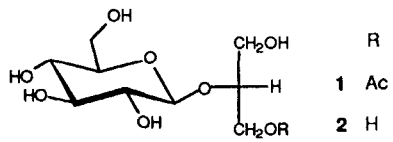
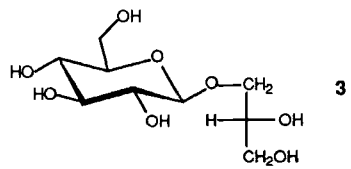
ABSTRACT: β-D-glucopyranosides, linked to C-2 or C-3 of the glycerol aglicone moiety, were unambiguously synthesized.

Japanese Authors reported the isolation of some naturally occurring glycerol glucosides from bulbs of the genus *Lilium* (lilioside A **1** and B **2** from *L. longiflorum*[1], lilioside C **3** from *L. lancifolium*[2] and lilioside D **4** and E **5** from *L. japonicum*[3].



R
1 Ac
2 H



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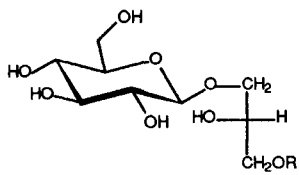
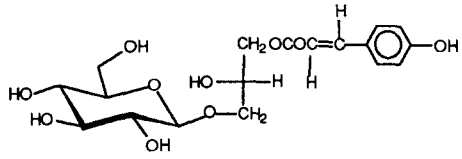


R
4 H
5 Ac

* To whom correspondence should be addressed

The occurrence of regaloside A **6** and B **7,** phenyl propanoid glycerol glucosides from *Lilium regale*, was also reported[4]. Similarly were isolated the *epi*-regaloside A **8** and *epi*-regaloside C **9** from *L. pardarinum*, *epi*-regaloside F **10** and regaloside G **11** from *L. auratum*[5] (the *epi*-regalosides were obtained as mixtures with the corresponding (2S)-regalosides). When these esters were submitted to alkaline methanolysis with 3% sodium methoxide in methanol, they were hydrolyzed to afford the corresponding methyl phenyl propanoate and the glycerol glucosides.



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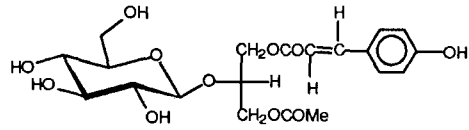

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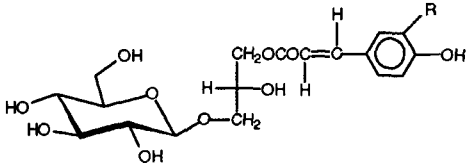
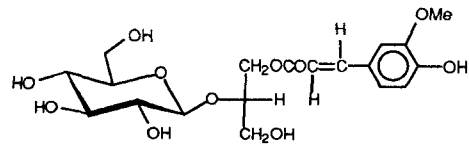


8 R = H

9 R = OH

10 R = OMe



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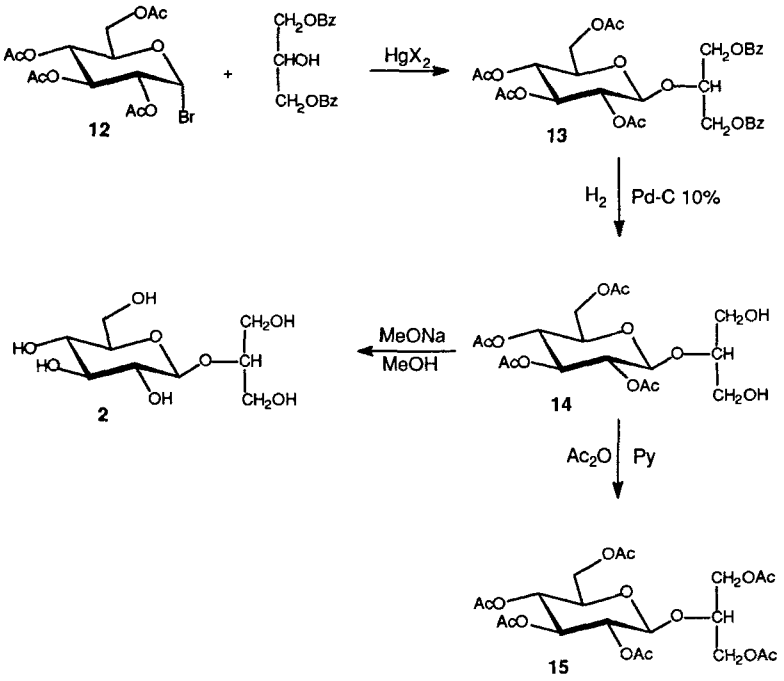
Liliosides and regalosides seemed till now to be characteristic constituents of the genus *Lilium*, and their structures appeared to vary depending on the species.

However, glycerol glucosides have been found also in different higher plants, although in small amounts[6].

The determination of these compounds in complex mixtures can be afforded by GC-MS analysis of acetylated samples, because of a typical fragmentation pathway common to liliosides[7].

Scheme 1

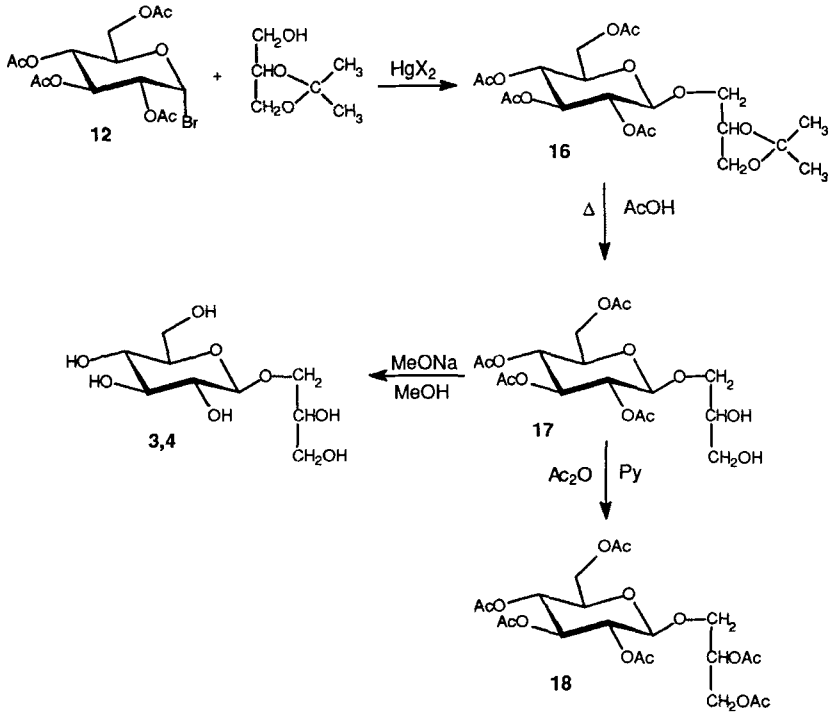


The availability of authentic samples would allow an easier identification by comparison. Only few studies on the synthesis of unsubstituted glycerol glycosides by coupling of a glycosyl donor with a proper glycerol derivative are reported in literature, regarding e. g. galactosyl[8] and lactosyl[9] glycerols. To the best of our knowledge, no synthesis of glucosyl glycerols have been published; moreover, the analytical and spectroscopic data relative to samples of them obtained from plants are not complete.

In order to make available valuable amounts of glycerol glucosides, we undertook an independent synthesis of 2-O-β-D-glucopyranosyl glycerol (lilioside B **2**) and a mixture of (2R) and (2S)-3-O-β-D-glucopyranosyl glycerols (lilioside C and D, **3+4**). Schemes 1 and 2 show the reaction sequence affording the desired products.

A simple variation of the classical Koenigs-Knorr reaction was sought.

Scheme 2



2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide **12** was reacted at room temperature with 1,3-dibenzyloxy-2-propanol in dry acetonitrile, in the presence of $Hg(CN)_2$ and $HgBr_2$ as catalysts. The work-up of the reaction mixture afforded the hitherto unknown crystalline compound **13** in high yields.

Deprotection of glycerol hydroxyl groups was achieved by catalytic hydrogenolysis (10% Pd-C) at room temperature and pressure, affording the hitherto unknown crystalline diol **14** in quantitative yield.

Surprisingly enough, the reaction was complete after ten minutes, instead of 20 hours previously reported[2,9].

Unsubstituted glucosyl glycerol **2** was obtained by hydrolysis of **14** with MeONa in methanol at room temperature, followed by treatment on Amberlite-IR 120 ion-exchange resin, whereas peracetylated **15** was obtained by reacting **14** with excess

Ac_2O in pyridine - M. ps of **2** and **15** were identical with those reported for the naturally occurring lilioside **2** and its acetylated derivative[1].

β-D-glucosyl glycerol **16** could be achieved as a 55:45 mixture (by GC) of the (S),(R) diastereoisomers by condensing **12** with D,L-1,2-O-isopropylidenglycerol in dry acetonitrile, in the presence of $Hg(CN)_2$ and $HgBr_2$ (optically pure 1,2-O-isopropylidenglycerol racemises[10] during the Koenigs-Knorr condensation procedure).

M.p. and TLC Rf of **16** ($CHCl_3$: MeOH 92:8) are in good agreement with those reported in literature[10] for 3-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-sn-glycerol-1,2-O-isopropylidene.

By 3 hours heating in acetic acid, 52:48 (S),(R) diastereomeric **17** can be obtained as a crystalline product, m.p. 92-3° C (3-O-2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-sn-glycerol from the literature[10] has m.p. 107-109°C and similar Rf (TLC $CHCl_3$: MeOH 90:10).

Unsubstituted diastereomeric (53:47) (S),(R) glucosyl glycerols **4** and **3** were obtained as a white amorphous powder by alkaline methanolysis of **17** and subsequent treatment with Amberlite-IR 120.

17 can be acetylated with Ac_2O-pyridine, affording the peracetylated **18** as a white powder, in a (S):(R) ratio 53:47.

^{1}H-NMR data of **18** are very similar to those reported for the (S), (R)-liliosides obtained by Sashida[5] after hydrolysis of regaloside and *epi*-regaloside A mixture.

In a similar way glycerols linked to different monosaccharides carrying free or variously substituted hydroxyl groups can be obtained.

EXPERIMENTAL

GENERAL METHODS. Melting points were taken using a Büchi 510 apparatus and are uncorrected. Elemental analyses were obtained on a C. Erba 1106 elemental analyzer. ^{1}H-NMR spectra were recorded on a Bruker ACE-300 instrument as solution in $CDCl_3$ (TMS as internal standard) or D_2O (water signal as i. s.); chemical shifts are expressed in δ, splitting patterns designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (J) are reported in Hz.

Infrared spectra (IR) were obtained as thin films (sodium chloride plates) on a Perkin-Elmer 197 spectrophotometer, and are reported in wave numbers (cm^{-1}). GC was performed with a C. Erba HRGC 5160 Mega Series gaschromatograph,

equipped with a flame ionization detector, and recorded with a SP 4290 Spectra Physics chromato-integrator. GC operating conditions were as follow. Column: a silica capillary column OV-1 bonded (25 m x 0.32 mm), 0.15 μm film tickness, Hewlett-Packard. Carrier gas: H_2, 0.3 Kg cm^{-2} pressure.

Programmed chromatographic separations were run using appropriate column temp. for sugars analysis (as TMSi-derivatives or as acetylderivatives): start temp. 100°; 8° min^{-1} to 250°; 10° min^{-1} to 310°, then held at 310° for 10 min.

Gas chromatography mass spectroscopy (GC-MS) was performed on a Hewlett-Packard 5890 GC with an HP 5970 Mass Selective Detector (EI), using a 25 m x 0.32 mm I.D. x 0.17 μm fused silica capillary column of 100% methylsilicon (HP-1 Hewlett-Packard), directly introduced into the ion source.

The GC-MS conditions were: initial temp. 100°, final temp. 310°, temp. rate 10°, inj. temp. 250°, det. temp. 280°. He was the carrier gas with a head pressure of 2.5-3.5 psi, 25 cm sec^{-1} linear velocity.

Mass spectra were acquired over 40-800 mass unit range at 1 scan sec^{-1} with ionizing electron energy 70 eV, electron current 0.3 mA, ion source 200°; the vacuum was 10^{-5} Torr. The samples were dissolved in suitable solvents and injected (1 μl) in a splitless mode.

All reactions were monitored by TLC carried out on Merck silica gel plates (60 F_{254}, 0.25 mm), and spots were visualized under UV (254 nm) illumination and by spraying the plates with a 1/1 aqueous sulfuric acid containing 3% of $K_2Cr_2O_7$, followed by heating.

2-Benzyloxy-1-[(benzyloxy)methyl]ethyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **13**

To a magnetically stirred solution of 1.8 ml (7.36 mmol) of 1,3-dibenzyloxy-2-propanol in 20 ml of dry acetonitrile, containing 1.46 g (4 mmol) of $HgBr_2$ and 1.02 g (4 mmol) of $Hg(CN)_2$, a solution of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide **12** (3.16 g, 7.6 mmol) in 20 ml of dry acetonitrile was added dropwise.

The reaction mixture was stirred for 19 h at room temperature, then monitored by TLC ($CHCl_3$: MeOH 98:2, where the major product had Rf 0.76).

The solution was evaporated; the residue was dissolved in $CHCl_3$ (70 ml) and washed with 1M KBr aqueous solution (3 x 30 ml), then with water (30 ml), in order to eliminate the catalysts. The organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure.

The colourless oil so obtained, cooled in ice-bath, was grinded with few drops of ethanol, giving **13** as crystalline solid.

The dibenzyloxy derivative was filtered off: 2.99 g (67% yield). Recrystallized from ethanol, had m.p. 55-56° C.

Elem. anal., found % (calcd for $C_{31}H_{38}O_{12}$): C, 61.93 (61.78); H, 6.38 (6.35).

^{1}H-NMR ($CDCl_3$), δ: 7.30 (m, aromatics), 5.20 (t, J 9.5 Hz, H-3'), 5.08 (t, J 9.5 Hz, H-4'), 5.00 (dd, J 8, 9.5 Hz, H-2'), 4.80 (d, J 8 Hz, H-1'), 4.53 (s, CH_2Ph), 4.51 (s, CH_2Ph), 4.22 (dd, J 5, 12 Hz, H-6'α), 4.08 (dd, J 2, 12 Hz, H-6'β), 4.04 (m, H-2), 3.66 (dd, J 5, 10.5 Hz, H-3α), 3.65 (dd, J 6.5, 10.5 Hz, H-1α), 3.63 (m, H-5'), 3.55 (dd, J 2.5, 10.5 Hz, H-3β), 3.53 (dd, J 1.5, 10.5 Hz, H-1β), 2.04, 2.01, 1.99, 1.93 (s, CH_3CO)

GC-MS: t_r 25.3 min. MS m/z (rel. intensity) 511 (1), 422 (1), 331 (20), 271 (15), 169 (50), 109 (22), 91 (100), 43 (80).

IR $\nu_{C=O}$ 1754 cm^{-1}

2-Hydroxy-1-[(hydroxy)methyl]ethyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **14**

Compound **13** (1 g, 1.8 mmol) was dissolved in methanol (30 ml), treated with 10% Pd-C (0.9 g) and shaken under hydrogen atmosphere. Hydrogen absorption, theoretical amount plus 10%, finished after 10 min. The catalyst was filtered off and the solvent evaporated under reduced pressure to yield **14** as colourless oil. TLC control ($CHCl_3$:MeOH 90:10) showed one spot with Rf 0.57. The residue, ice-bath cooled, was grinded with few drops of ethanol, affording white crystalline solid (0.73 g, 97% yield). Recrystallized from ethanol, had m.p. 101- 102° C.

Elem. anal., found % (calcd for $C_{17}H_{26}O_{12}$): C, 48.27 (48.34); H, 6.24 (6.20).

^{1}H-NMR ($CDCl_3$), δ: 5.26 (t, 9.5 Hz, H-3'), 5.04 (t, J 9.5 Hz, H-4'), 5.03 (dd, J 8, 9.5 Hz, H-2'), 4.67 (d, J 8 Hz, H-1'), 4.25 (dd, J 2.5, 12 Hz, H-6'α), 4.13 (dd, J 6.5, 12 Hz, H-6'β), 3.85-3.75 (m, H-5', H-2), 3.68-3.58 (m, 2 H-1, 2 H-3), 2.90 (t, J 8 Hz, OH), 2.15-2.00 (s, CH_3CO), 1.90 (t, J 8 Hz, OH).

GC-MS (as TMSi-derivative): t_r 13.4 min. MS m/z (rel. intensity) 422 (0.5), 331 (7), 271 (3), 219 (4), 218 (7), 169 (20), 131 (15), 103 (40), 81 (8), 73 (80), 43 (100).

IR $\nu_{C=O}$ 1740 cm^{-1}, ν_{OH} 3340 cm^{-1}

2-Hydroxy-1-[(hydroxy) methyl] ethyl β-D-glucopyranoside **2**

Intermediate **14** (0.22 g, 0.52 mmol) was dissolved in methanol (10 ml) and a 1

% sodium methoxide solution (14 ml) was added. The reaction was monitored by TLC ($CHCl_3$:MeOH 90:10) until the starting material was totally consumed. After 18 h under stirring at room temp., the reaction was complete. The solution was neutralized with Amberlite IR-120 ion-exchange resin. The resin was filtered off, washed with methanol and the solvent was evaporated *in vacuo*, to afford **2** as white solid (0.12 g, 90 % yield), m.p. 166-167° C (lit[1] 166-167° C). **2** had Rf 0.32 in TLC (butanol 45/acetic acid 30/diethyl ether 15/water 5).

^{1}H-NMR (D_2O), δ: 4.51 (d, J 8 Hz, H-1'), 3.82-3.41 (m, 2 H-6', 2 H-1, 2 H-3, H-2), 3.40 (t, J 9 Hz, H-3'), 3.36 (m, H-5'), 3.28 (t, J 9 Hz, H-4'), 3.21 (dd, J 8, 9 Hz, H-2').

GC-MS (as TMSi-derivative): t_r 13 min. MS m/z (rel. intensity) 451 (1), 361 (5), 337 (1), 219 (7), 204 (100), 191 (11), 147 (44), 129 (15), 103 (46), 73 (100).

IR ν_{OH} 3340 cm^{-1}

2-Acetyloxy-1-[(acetyloxy)methyl]ethyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **15**

To a solution of 0.2 g (0.47 mmol) of intermediate **14** in pyridine at room temp., excess acetic anhydride (3 ml) was added. The reaction mixture was left overnight, then was poured with stirring into crushed ice (5 g). As white crystalline solid **15** separated out and was filtered off: 0.2 g (87 % yield), m.p. 127-128° C (lit[1] 128° C). TLC analysis ($CHCl_3$:MeOH 90:10) showed a single spot having Rf 0.76.

^{1}H-NMR ($CDCl_3$), δ: 5.18 (t, J 10 Hz, H-3'), 5.05 (t, J 10 Hz, H-4'), 4.96 (dd, J 8, 10 Hz, H-2'), 4.42 (d, J 8 Hz, H-1'), 4.08-4.24 (m, 2 H-1, 2 H-3, 2 H-6'), 4.05 (m, H-2), 3.68 (ddd, J 2.5, 5, 10 Hz, H-5'), 2.07, 2.06, 2.04, 2.00, 1.98 (s, CH_3CO).

GC-MS: t_r 14.6 min. MS m/z (rel. intensity) 447 (1), 331 (3), 271 (2), 169 (10), 159 (54), 145 (7), 115 (6), 103 (3), 43 (100).

IR $\nu_{C=O}$ 1761 cm^{-1}

3-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,2-O-isopropyliden-glycerol **16**

To a magnetically stirred solution of 0.45 ml (3.68 mmol) of D,L-2,3-isopropylidenglycerol, 0.73 g (2 mmol) of $HgBr_2$ and 0.51 g (2 mmol) of $Hg(CN)_2$ in 10 ml of dry acetonitrile, a solution of 1.58 g (3.8 mmol) of **12** in 10 ml of dry acetonitrile was added dropwise, during 30 minutes. The reaction mixture was stirred at 20°C for 2h. The completion of the reaction was followed by TLC ($CHCl_3$:MeOH 92:8), having the reaction product Rf 0.67 (lit[10] 0.68).

The solution was evaporated; the resulting oil was dissolved in $CHCl_3$ (60 ml), washed with 1M KBr aqueous solution (2 x 30 ml), then with water (30 ml).

Drying over anhydrous Na_2SO_4, filtration and evaporation afforded a colourless oil that was grinded with diisopropyl ether; **16** was obtained as white crystalline solid (1.41 g, 83% yield), m.p. 108-110° C (lit.[10] 110-111° C).

^{1}H-NMR ($CDCl_3$), δ: 5.22 (t, J 9.5 Hz, H-3' (S)), 5.20 (t, J 9.5 Hz, H-3' (R)), 5.09 (t, J 9.5 Hz, H-4' (S)), 5.08 (t, J 9.5 Hz, H-4' (R)), 5.01 (dd, J 8, 9.5 Hz, H-2' (R)), 5.00 (dd, J 8, 9.5 Hz, H-2' (S)), 4.62 (d, J 8 Hz, H-1' (R)), 4.59 (d, J 8 Hz, H-1' (S)), 4.3-3.6 (m, 2 H-6', H-5', 2 H-3, H-2, 2 H-1), 2.09, 2.05, 2.02, 2.00 (s, CH_3CO), 1.401 (s, CH_3(R)), 1.40 (s, CH_3 (S)), 1.30 (s, CH_3 (S,R)).

GC-MS: t_r 13.2 min. MS m/z (rel. intensity) 447 (9), 331 (1), 169 (24), 145 (33), 127 (11), 115 (43), 101 (74), 43 (100).

IR $\nu_{C=O}$ 1750 cm^{-1}

3-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-propane-1,2-diol **17**

A solution of 0.8 g (1.73 mmol) of **16** in acetic acid (70 ml) was heated to 50° for 3 h. After disappearance of **16**, followed by TLC, and appearance of a new product which had Rf 0.34 in $CHCl_3$:MeOH 90:10 (lit[10] 0.34), the solvent was evaporated under reduced pressure, giving a colourless oil. **17** was obtained as white crystalline solid grinding the residue with diethyl ether and light petroleum ether (0.68 g, 93 % yield), m.p. 102-103° C (lit[10] 107-109° C).

^{1}H-NMR ($CDCl_3$), δ: 5.30 (t, J 9.5 Hz, H-3'), 5.07 (t, J 9.5 Hz, H-4'), 5.011 (dd, J 9.5 Hz, H-2' (R)), 5.01 (dd, J 8, 9.5 Hz, H-2' (S)), 4.55 (d, J 8 Hz, H-1'), 4.21 (m, 2 H-6'), 3.91-3.55 (m, H-5', 2 H-3, H-2, 2 H-1), 2.11, 2.07, 2.04, 2.02 (s, CH_3CO).

GC-MS (as TMSi-derivative): t_r 13.9 min. MS m/z (rel. intensity) 511 (1), 331 (6), 271 (4), 219 (3), 169 (20), 145 (40), 73 (80), 43 (100).

IR $\nu_{C=O}$ 1755 cm^{-1}, ν_{OH} 3500 cm^{-1}

3-O-(β-D-glucopyranosyl)-propane-1,2-diol **3,4**

Acetylated **17** (0.2 g, 0.474 mmol) was hydrolyzed as described for **14**. Similar work-up afforded a mixture of **3,4** as white solid, m.p. 93-95° C (0.11 g, 91 % yield). TLC (butanol 45/acetic acid 30/diethyl ether 15/water 5) showed a spot having Rf 0.32 for the polar unsubstituted **3,4**.

^{1}H-NMR (D_20), δ: 4.38 (d, J 8 Hz, H-1' (S)), 4.37 (d, J 8 Hz, H-1' (R)), 3.91-

3.45 (m, 2 H-6', 2 H-3, H-2, 2 H-1), 3.38 (t, J 9 Hz, H-3'), 3.35 (ddd, J 2, 6, 9 Hz, H-5'), 3.27 (t, J 9 Hz, H-4'), 3.19 (dd, J 8, 9 Hz, H-2')

GC-MS (as TMSi-derivative): t_r 13.5 min. MS m/z (rel. intensity) 491 (1), 451 (2), 361 (5), 337 (8), 219 (5), 205 (18), 204 (99), 147 (26), 129 (11), 103 (17), 73 (100).

IR ν_{OH} 3450 cm^{-1}

3-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1,2-di-O-acetoxy-propane **18**

The peracetylated **18** was obtained by reacting the intermediate **17** (0.21 g, 0.49 mmol) as previously described for **14**: 0.21 g (87 % yield), m.p. 93-95° C, Rf 0.76 in $CHCl_3$:MeOH 90:10 TLC analysis.

^{1}H-NMR ($CDCl_3$),δ: 5.20 (t, J 9.5 Hz, H-3' (R)), 5.19 (t, J (9.5 Hz, H-3' (S)), 5.17 (m, H-2), 5.08 (t, J 9.5 Hz, H-4' (R)), 5.07 (t, J 9.5 Hz, H-4' (S)), 5.04 (dd, J 8, 9.5 Hz, H-2' (R)), 5.03 (dd, J 8, 9.5 Hz, H-2' (S)), 4.54 (d, J 8 Hz, H-1' (R)), 4.53 (d, J 8 Hz, H-1' (S)), 4.29 (dd, J 6, 12 Hz, H-1α (S)), 4.27 (dd, J 4, 12 Hz, H-1α (R)), 4.26 (dd, J 5, 12 Hz, H-6'α (R)), 4.25 (dd, J 5, 12 Hz, H-6'α (S)), 4.13 (dd, J 2.5, 12 Hz, H-6'β (R, S)), 4.12 (dd, J 6, 12 Hz, H-1β (S)), 4.09 (dd, J 4.5,11 Hz, H-1β (R)), 3.96 (dd, J 5, 11 Hz, H-3α (S)), 3.95 (dd, J 5, 11 Hz, H-3α (R)), 3.70 (dd, J 4, 5 Hz, H-3β (S)), 3.69 (m, H-5'), 3.68 (dd, J 5.5, 11 Hz, H-3β (R)), 2.10, 2.09, 2.08, 2.07, 2.06, 2.055, 2.03, 2.01 (s, CH_3CO).

GC-MS: t_r 14.9 min.MS m/z (rel. intensity) 433 (1), 331 (2), 169 (9), 159 (91), 145 (18), 115 (10), 98 (10), 43 (100).

IR $\nu_{C=O}$ 1745 cm^{-1}

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REFERENCES

(1) Kaneda, M., Mizutani, K., Takahashi, Y., Kurono, G. and Nishikawa, Y., *Tetrahedron Lett.*, **1974**, 3937.

(2) Kaneda, M., Mizutani, K. and Tanaka, K., *Phytochemistry*, 1982, **21**, 891.

(3) Kaneda, M., Kobayashi, K., Nishida, K. and Katsuta, S., *Phytochemistry*, 1984, **23**, 795.

(4) Shimomura, H.,Sashida, Y., Mimaki, Y. and Iida, N., *Phytochemistry*, 1988, **27**, 451.

(5) Shimomura, H., Sashida, Y., Mimaki, Y., Kudo, Y. and Maeda, Y., *Chem. Pharm. Bull.*, 1988, **36**, 4841.

(6) Patritti, G., Degree Dissertation, University of Pavia, 1993; Rovati, M., Degree Dissertation, University of Pavia, 1993.

(7) Marinone Albini, F., Murelli, C., Patritti, G. and Rovati, M., unpublished results.

(8) Austin, P. W., Hardy, F. E., Buchanan, J. G., and Baddiley, J., *J. Chem. Soc.* **1965**, 1419.

(9) Hronowsky, L.J.J., Szarek, W.A., Hay, G.W., Krebbs, A. and Depew, W.T., *Carbohydr. Res.*, 1991, **219**, 33.

(10) Van Boeckel, C.A.A., Visser, G.M. and Van Boom J.H., *Tetrahedron*, 1985, **41**, 4557.

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