Tetrahedron Vol. 45, No. 5, pp. 1355 to 1364, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00
Pergamon Press plc

PARTIAL SYNTHESIS OF SOME PHYSIOLOGICALLY RELEVANT GIBBERELLIN GLUCOSYL CONJUGATES

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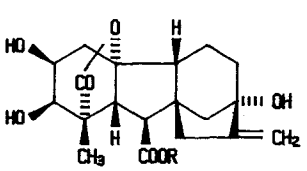
(*Received in Germany* 20 *July* 1988)

Abstract - GA_8-2-O-ß-D-glucoside (4d), GA_8-13-O-ß-D-glucoside (5c) and GA_{20}-13-O-ß-D-glucoside (6c) could be obtained by partial synthesis. Synthetic 4d was compared with isolated GA_8-2-O-ß-D-glucoside[1] in order to confirm its structure. In addition, the syntheses of ß-D-glucosyl esters of GA_7 (7b), GA_8 (8b) and GA_{20} (9b) are described.

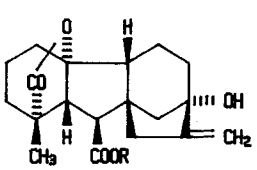
INTRODUCTION

GA_8-2-O-ß-D-glucoside (4d)+ has been isolated from pods of *Phaseolus coccineus* as the first conjugate of gibberellins[1,2]. The structural elucidation of 4d and of subsequently identified gibberellin glucosides from plant (Ref. see Lit.[5]) was based on spectroscopical data of the intact compounds, their derivatives or on investigations with parts of them after hydrolysis.

We now report on the partial synthesis of GA_8-O-glucosides for comparison reasons in order to finally confirm the structure of the endogenous specimen. With the same synthetic approach we also tried to synthesize glucosyl derivatives of GA_{20} and some gibberellin glucosyl esters which are necessary for identification purposes in metabolic studies[6,7,8] and for the identification of putative gibberellin conjugates from plant.



1a : R = H
1b : R = Me



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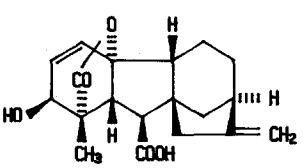

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+Numbering of the C-skeleton is based on the ent-gibberellane[3]. The name GA_8-3(O)-ß-D-glucoside, which was formely used for 4d in the literature[4], was derived from the gibbane nomenclature[1].

RESULTS AND DISCUSSION

The main problem in the chemical glucosylation of GA_8 (1a) consists in the multifunctionality of the molecule. Thus, if GA_8 methyl ester 1b was subjected to the Koenigs-Knorr reaction[9,10,11] we were to expect isomeric GA_8-O-(2,3,4,6-tetra-O-acetyl)-glucosyl derivatives. The reaction mixture was deacetylated by sodium methoxide. The resulting isomeric O-glucosyl-GA_8-methyl esters were re-acetylated (short term). By this, differences in the reactivity of free hydroxy groups of GA_8 (2-O, 3-O, 13-O) lead to different acetates of the glucosides that could be separated by silica gel chromatography (s. Fig. 1)[11].

In the ^{1}H-NMR spectrum of the pentaacetate fraction (m/z = 750), besides the 5 acetyl singulets at 1.987, 2.028, 2.060, 2.083 and 2.140 ppm, the downfield shifted signal of the 3-H (5.257, d, $J_{3,2}$ ≈ 4 Hz) could be observed whereas the 2-H signal was unaffected at 3.863 ppm (Tab. 1). From these data it can be derived that the 3-hydroxy group of GA_8 is acetylated but not the more reactive 2-hydroxy group[5]. This only suits the structure of a 3-O-acetyl-2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl-GA_8-methyl ester 4b for the pentaacetate.

The tetraacetate fraction (needles, mp. 212-215°C, m/z = 708) shows in the NMR unshifted signals for both the 2- and 3-hydroxy group (3.76, 3.86 ppm). As the substance could be transformed into 4b by prolonged acetylation, its structure has to be the 2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl-GA_8-methyl ester 4a. Deacetylation of 4a led to 2-O-ß-D-glucopyranosyl-GA_8-methyl ester 4c showing an M-1 ion in the negative ionization MS (m/z = 539). In the NMR spectra the unchanged positions of the 18-H_3- and 17-H_2-signals indicate that the glucosyl moiety is attached neither to the 3-nor to the 13-hydroxy group[5]. Treatment of 4c with lithium-S-propyl thiolate resulted in the free GA_8-2-O-ß-D-glucopyranoside 4d ($[\alpha]_D^{26}$ -0.6°)+, the NMR spectrum of which was identical with that of isolated 4d. Further evidence for the identity of synthesized 4d with endogenous 4d was gained from comparing their acetates 4e and 4f. The NMR spectrum of synthetic 3-O-acetyl-GA_8-2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucoside 4f (mp. 257-260°C, $[\alpha]_D$ -1.2°) coincides with that of 4f obtained from isolated 4d (Lit.[1] mp. 249°C, $[\alpha]_D$ -2.6°). The mixed mp. 257-259°C did not show any depression. The same comes true for the GA_8-2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucoside 4e for which identical melting points and mixed mp. 236-239° as well as identical NMR- and MS-spectra could be obtained.

Besides the tetraacetate 4a and the pentaacetate 4b from the acetylation mixture of O-glucosyl-GA_8-methyl esters (see Fig. 1) we also isolated a hexa-acetate fraction (m/z = 792). On the basis of NMR, its structure was attributed to 2,3-di-O-acetyl-13-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl-GA_8-methyl ester 5a. Its deacetylation resulted in 13-O-ß-D-glucosyl-GA_8-methyl ester (5b, $[\alpha]_D^{29}$ +32.5°). The downfield shift of the 17-H_2 signals in the NMR-spectrum of 5b (4.98 and 5.34 ppm) indicates the neighbourhood of the 13-O-glucosyl moiety. The free GA_8-13-O-ß-D-glucoside 5c ($[\alpha]_D^{27}$ +20.2°) was obtained by

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+The difference in the $[\alpha]_D$ values (Lit.[1] $[\alpha]_D$ +6.7°) was reinvestigated with HPLC-purified substance resulting in agreeable data: isolated 4d $[\alpha]_D^{20}$ -0.4°.

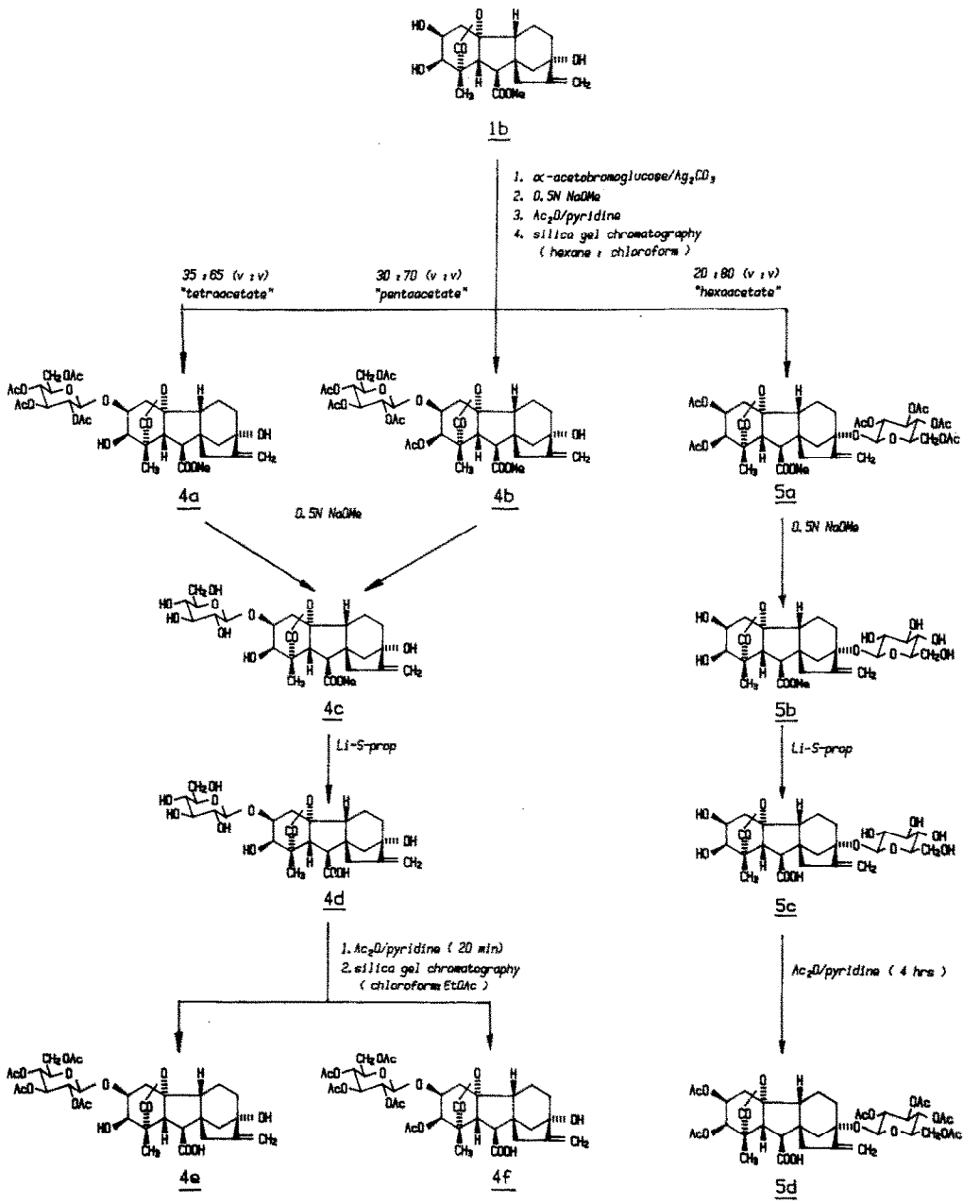


Fig. 1: Scheme of the synthesis of isomeric GA_8-O-β-D-glucopyranosides

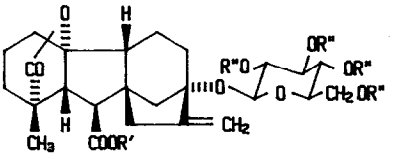
Tab. 1 ^{1}H-NMR Data (ppm) of GA_8-2-O-glucoside (4d), GA_8-13-O-glucoside (5c), and GA_{20}-13-O-glucoside (6c) as well as of their derivatives (TMS internal standard, v = 100 MHz $CDCl_3$, w = 360 MHz $CDCl_3$, x = 100 MHz D_6-acetone + 10 % D_2O, y = 200 MHz $CDCl_3$, z = 200 MHz D_6-acetone + 10 % D_2O)

Compound	2-H (ddd) (J=10, 6, 4 Hz)	3-H (d) (J=4 Hz)	5-H (d) (J=10.5 Hz)	6-H (d) (J=10.5 Hz)	17-H_2 (m)	18-H_3 (s)	OCH_3 (s)	1'-H (d) (J=7.5 Hz)	acetates (ss)
4a[v]	3.86(m)	3.76(m)	3.33	2.63	4.97/5.27	1.20	3.72	4.60	2.00,2.02,2.06,2.08
4b[w]	3.863	5.257	3.228	2.626	4.975/ 5.276	1.043	3.725	4.507	1.987,2.028,2.060, 2.083,2.140
4c[x]	3.85(m)	3.72	3.23	2.58	4.88/5.20	1.14	3.74	4.56	---
4d[x]	3.84(m)	3.70	3.28	2.57	4.94/5.19	1.25	-	4.58	---
4e[w]	3.856	3.771	3.292	2.682	4.975/ 5.272	1.256	-	4.565	2.011,2.036,2.072, 2.090
4f[v]	3.87(m)	5.25	3.19	2.62	4.98/5.28	1.06	-	4.54	1.97,2.01,2.04,2.08, 2.11
5a[v]	4.95(m)	5.24	3.30	2.62	5.00/5.28	1.06	3.74	4.66	1.97,2.00,2.02,2.04, 2.06,2.17
5b[x]	3.82(m)	3.68	3.33	2.56	4.98/5.34	1.06	3.69	4.51	---
5c[x]	3.80(m)	3.65	3.30	2.55	5.03/5.38	1.17	-	4.56	---
5d[v]	4.96(m)	5.28	3.28	2.63	5.03/5.29	1.11	-	4.67	1.96,1.99,2.02,2.05, 2.06,2.15
			5-H (d) (J=10 Hz)	6-H (d) (J=10 Hz)	17-H_2 (m)	18-H_3 (s)	OCH_3(s)	1'-H (d) (J=7,7 Hz)	acetates (ss)
6a[y]			2.64	2.54	4.99/5.21	1.07	3.70	4.57	2.000,2.020,2.042, 2.063
6b[z]			2.617	2.565	4.925/ 5.301	0.993	3.694	4.486	----
6c[z]			2.610	2.562	4.953/ 5.322	1.130	-	4.553	----
6d[y]			2.620	2.530	5.050/ 5.236	1.136	-	4.575	2.009,2.030,2.054, 2.071

demethylation of 5b. Its structure was confirmed by NMR data of the hexaacetate 5d ($[\alpha]_D^{27}$ +34.8°) produced from 5c by short term acetylation. The signals of the 2-O- and 3-O-acetates (1.96 and 2.15 ppm) together with the downfield shift of the 2-H and 3-H (4.96 and 5.28 ppm) coincide with the structure.

So far, the performed glucosylation of GA_8-methyl ester (1b) led to 2-O- and 13-O-glucosylation. But, there was no evidence for simultaneous glucosylation of the axial 3-hydroxy group.

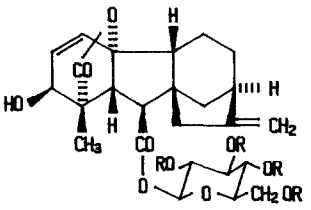
The glucosylation of the tertiary 13-hydroxy group of 1b is in agreement with former experiences[10,11,12] and could also be observed for GA_{20}-methyl ester 2b, from which 13-O-ß-D-glucopyranosyl-GA_{20}-methyl ester 6b ($[\alpha]_D$ +39.6°) could be obtained with 39.8 % yield. In the NMR spectrum of 6b the typical shift of the 17-H_2-signals (4.925 and 5.301 ppm) for 13-O-glucosyl structure is apparent. The corresponding tetraacetate 6a ($[\alpha]_D$ +48.7°) is characterized by its molecular ion at m/z = 676 as well as by 4 acetate singulet s at 2.000, 2.020, 2.042 and 2.063 ppm in the NMR spectrum. From the methyl ester 6b the free GA_{20}-13-O-ß-D-glucopyranoside (6c, $[\alpha]_D^{28}$ -36.6°) could be obtained. Its structure was confirmed by spectroscopical data of the GA_{20}-13-O-ß-(2,3,4,6-tetra-O-acetyl)-glucoside 6d, ($[\alpha]_D^{28}$ +39.9°). The NMR spectrum of 6d shows typical signals at 4.575 (d, $J_{1',2}$ = 7.68 Hz, 1'-H), 2.009, 2.030, 2.054 and 2.070 ppm (4s, acetates).



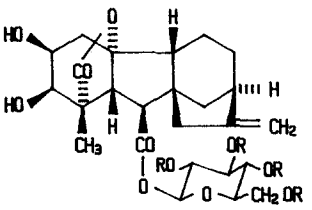
	R'	R"
6a :	Me	Ac
6b :	Me	H
6c :	H	H
6d :	H	Ac

GA_{20}-13-O-ß-D-glucoside 6c has not yet been isolated from plant, but its metabolic formation in various plant tissues after feeding of GA_{20} (2a) could be demonstrated on the basis of this synthetic standard[6,7,13]

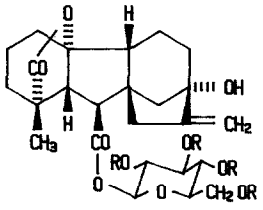
For our metabolic work we also need gibberellin-O-ß-D-glucosyl esters, which represent another group of endogenous GA conjugates[5,13]. Thus, by reacting the free acidic GA_7 (3), GA_8 (1a) and GA_{20} (2a) with equimolar amounts of α-acetobromoglucose we obtained the corresponding GA-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl esters 7a, 8a, 9a with 50 to 60 % yield. The crucial step of their deacetylation by sodium methoxide requires dedicated conditions in order to cut down transesterfication. The physical data of the synthesized glucosyl esters of GA_7 7b, GA_8 8b and GA_{20} 9b as well as those of their acetates are summarized in Tab. 2.



7a : R = Ac
7b : R = H



8a : R = Ac
8b : R = H



9a : R = Ac
9b : R = H

Tab. 2 Physical data of synthesized gibberellin-O-ß-D-glucosyl esters and their tetraacetates (200 MHz ^{1}H-NMR, TMS internal standard, $CDCl_3$ (GA_7-GE(ac)$_4$, D_6-acetone (GA_7-GE)).

Compound	melting point	18-H_3(s)	5-H(d) J=10.5 Hz	6-H(d) J=10.5 Hz	17-H_2(m)	1'-H(d) J=7.9Hz	acetates (s)
GA_7-GE(ac)$_4$(7a)	164-165°C	1.199	3.131	2.773	4.805/ 4.960	5.750	1.994, 1.999, 2.015, 2.032
GA_7-GE(7b)	234-235°C	1.150	3.211	2.765	4.810/ 4.908	5.472	-
GA_8-GE(ac)$_4$(8a)	152-154°C	1.165	3.250	2.660	4.936/ 5.273	5.812	2.024, 2.037, 2.050, 2.091
GA_8-GE(8b)	amorphous	1.105	3.262	2.631	4.834/ 5.144	5.489	-
GA_{20}-GE(ac)$_4$(9a)	142-144°C	1.038	2.698	2.521	4.925/ 5.271	5.798	1.999, 2.021, 2.045, 2.069
GA_{20}-GE(9b)	amorphous	1.027	2.689	2.608	4.840/ 5.174	5.535	-

EXPERIMENTAL

All melting points are corrected. The ^{1}H-NMR spectra were measured with an 100 MHz Varian, a 200 MHz or a 360 MHz Bruker equipment, respectively. Negative and positive ionization mass spectra were obtained with the mass spectrograph according to M. v. Ardenne.

The preparative HPLC was performed with an Hewlett Packard HP 1090 equipped with a 10 x 250 mm column Lichrosorb RP 18, 7 µm (Merck) and MeOH:H_2O = 25:75 (4 ml/min) as solvent (210 nm detection).

The general procedure of glucosylation including experimental conditions of deacetylation, acetylation, demethylation as well as chromatographic techniques was described in Lit.[9,10]

1. Glucosylation of GA_8-methyl ester (1b)

1.11 g GA_8-methyl ester (1b)[14] in dichlorethane were reacted with 5.6 g α-acetobromoglucose in presence of 11.4 g Ag_2CO_3/Celite. The reaction product was deacetylated by 0.5 N sodium methoxide and the resulting O-glucosyl-GA_8-methyl ester purified by chromatography on silica gel. After short term acetylation of this fraction (476 mg) with acetanhydride/pyridine the acetates were separated on silica gel with increasing concentration (5 % steps) of $CHCl_3$ within hexane. With 65 % $CHCl_3$ 78 mg (3.8 % total yield) of amorphous 2,3-di-O-acetyl-13-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl-GA_8-methyl ester 5a ($[\alpha]_D^{25}$ = +27.6° (0.49 ethanol), $C_{38}H_{48}O_{18}$, M^+ 792 m/z, ^{1}H-NMR see Tab. 1) were separated. The fraction with 70 % $CHCl_3$ within hexane contained 66 mg (3.0 % total yield) of amorphous 3-O-acetyl-2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl-GA_8-methyl ester 4b ($[\alpha]_D^{25}$ = +12.4° (0.38 ethanol), $C_{36}H_{46}O_{17}$, M^+ = 750 m/z, M^- = 750 m/z, $\nu_{max}^{CHCl_3}$ 1738 (ester-CO), 1775 (γ-lactone) cm^{-1}, ^{1}H-NMR see Tab. 1). With 80 % $CHCl_3$ within hexane 74 mg (3.5 % total yield) of 2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl-GA_8-methyl ester 4a ($[\alpha]_D^{30}$ -6.4° (0.43 ethanol), mp. 212-215°C, $C_{34}H_{44}O_{16}$, M^+ = 708 m/z, ^{1}H-NMR see Tab. 1) were eluted.

1.1. GA_8-2-O-ß-D-glucopyranoside (4d)

65 mg of the tetraacetate 4a were deacetylated by 0.5 N sodium methoxide resulting in 40 mg (92 %) amorphous 2-O-ß-D-glucopyranosyl-GA_8-methyl ester 4c, ($[\alpha]_D^{28}$ +2.1° (0.38 ethanol), after HPLC purification $[\alpha]_D^{27}$ +0.9° (0.45 ethanol), $C_{26}H_{36}O_{12}$, M^--1 = 539 m/z, ^{1}H-NMR see Tab. 1). Demethylation of 36 mg methyl ester 4c by lithium S-propyl thiolate afforded after chromatography on silica gel and DEAE-Sephadex 23 mg (69 %) amorphous (GA_8-2-O-ß-D-glucopyranoside 4d ($[\alpha]_D^{25}$ -1.9° (0.44 ethanol), after HPLC purification $[\alpha]_D^{26}$ -0.5° (0.43 ethanol), ^{1}H-NMR see Tab. 1).

By short term acetylation (acetanhydride/pyridine 20 min) of 30 mg of GA_8-2-O-ß-D-glucopyranoside 4d two acetates were obtained after separation by silica gel chromatography with a gradient of ethyl acetate within chloroform. At first,

13 mg (32 % yield) of 3-O-acetyl-GA_8-2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranoside 4f (needles from ethyl acetate/hexane, mp. 257-260°C (Lit.[1] mp. 249°C) mixed mp. 257-259°C, $[\alpha]_D^{26}$ -1.2° (0.41 ethanol) (Lit.[1] $[\alpha]_D$ -2.6°), $C_{35}H_{44}O_{17}$, M^--1 = 735 m/z, $\nu_{max}^{CHCl_3}$: 1714 (acid-CO), 1745-1762 (acetate-CO), 1780 (γ-lactone-CO) cm^{-1}, ^{1}H-NMR see Tab. 1), were eluted followed by 18 mg (63 % yield) of the GA_8-2-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranoside 4e (needles from ethyl acetate/hexane, mp. 236-239°C, $[\alpha]_D^{30}$ -21.0° (0.33 ethanol) ($C_{33}H_{42}O_{16}$, M^--1 = 693 m/z). The tetraacetate 4e from endogenous 4d showed mp. 236-239°C, mixed mp. 236-239°C, $[\alpha]_D^{25}$ -19.5° (0.42 ethanol).

1.2. GA_8-13-O-ß-D-glucopyranoside 5c

56 mg of the hexaacetate methyl ester 5a were deacetylated by 0.5 N sodium methoxide resulting in 33 mg (87 % yield) amorphous 13-O-ß-D-glucopyranosyl-GA_8-methyl ester 5b ($[\alpha]_D^{29}$ +32.5° (0.45 ethanol), $C_{26}H_{36}O_{12}$, M^--18 = 522 m/z, ^{1}H-NMR see Tab. 1).

From the methyl ester 5b (37 mg) the free GA_8-13-O-ß-D-glucopyranoside 5c could be obtained by demethylation with lithium-S-propyl thiolate in 70 % yield ($[\alpha]_D^{27}$ -20.2° (0.46 ethanol), ^{1}H-NMR see Tab. 1). By short term acetylation (acetanhydride/pyridine, 4 hrs) 5c could be transformed into a hexaacetate: 2,3-di-O-acetyl-GA_8-13-O-ß-D-(2,3,4,6-tetra-O-acetyl-glucopyranoside 5d (38 mg, 72 % yield), amorphous, $[\alpha]_D^{28}$ +34.8° (0.40 ethanol), $C_{37}H_{46}O_{13}$, M^--1 = 777 m/z; ^{1}H-NMR see Tab. 1).

Treatment of 5d with diazomethane led to the corresponding methyl ester 5a (see above).

2. Glucosylation of GA_{20}-methyl ester (2b)

560 mg of GA_{20}-methyl ester (2b) were reacted with 3.5 g α-acetobromoglucose in presence of 7.0 g Ag_2CO_3/Celite in dichloroethane. The reaction mixture was deacetylated by 0.5 N sodium methoxide and chromatographed on silica gel with chloroform/methanol. Beside 220 mg of starting material (2b), 322 mg (39.8 % total yield) 13-O-ß-D-glucopyranosyl-GA_{20}-methyl ester 6b ($[\alpha]_D^{28}$ +39.6° (0.60 ethanol), $C_{26}H_{36}O_{10}$, M^--1 = 507 m/z, M^++1 = 509 m/z, ^{1}H-NMR see Tab. 1) were isolated.

Acetylation of methyl ester 6b with acetanhydride/pyridine (4 hrs) and subsequent chromatography resulted in the 13-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl-GA_{20}-methyl ester 6a (amorphous, $[\alpha]_D^{28}$ +48.7° (c = 0.44 ethanol), $C_{34}H_{44}O_{14}$, M^+ = 676 m/z, M^--1 = 675 m/z, ^{1}H-NMR see Tab. 1).

The 13-O-ß-D-glucopyranosyl-GA_{20}-methyl ester 6b (300 mg) was demethylated by lithium-S-propyl thiolate. After column chromatography on silica gel and DEAE-Sephadex 226 mg (77.5 % yield) of GA_{20}-13-O-ß-D-glucopyranoside 6c ($[\alpha]_D^{28}$ +30.6° (0.50 ethanol), ^{1}H-NMR see Tab. 1) could be obtained.

The acetylation of GA_{20}-13-O-glucoside 6c (60 mg) with acetanhydride/pyridine yielded 68 mg (85 % yield) of GA_{20}-13-O-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranoside 6d ($[\alpha]_D^{28}$ +39.9° (0.50 ethanol), $C_{33}H_{42}O_{14}$, M^- = 662 m/z, M^+ = 662 m/z, ^{1}H-NMR see Tab. 1).

3. Synthesis of gibberellin glucosyl ester

The subsequently described procedure for the synthesis of GA_{20}-glucosyl ester is to consider as general example for the synthesis of gibberellin glucosyl esters listed in Tab. 2.

GA_{20} 2a (50 mg, 0.15 mmol) in 4 ml dichloroethanewas reacted with 65 mg (0.16 mmol) of α-acetobromoglucose in the presence of 95 mg (0.17 mmol) Ag_2CO_3/Celite at boiling temperature. After 10 min the mixture was filtered. After evaporation the residue was chromatographed on 15 ml DEAE-Sephadex A 25. The column was eluted with 15 ml aliquots of methanol, 0.5 N HOAc/methanol, 1.0 N HOAc/methanol; 5 ml fractions were collected. Fractions 3-5 contained the neutral component which was rechromatographed on 8 g silica gel (petrol ether/ethyl acetate) resulting in 48 mg GA_{20}-ß-D-(2,3,4,6-tetra-O-acetyl)-glucopyranosyl ester 9a (49 % yield, mp. 142-144°C, $C_{33}H_{42}O_{14}$, M^+ = 662 m/z, ^{1}H-NMR s. Tab. 2). Fractions 11-12 contained 25 mg (48 %) starting material 2a.

28 mg GA_{20}-ß-D-(2,3,4,6-tetra-O-acetyl)-glucosyl ester 9a (0.04 mmol) within 1 ml methanol were treated with 30 µl 0.5 N sodium methoxide for 5 min at room temperature. The reaction was stopped by 30 µl HOAc and the crude reaction mixture was separated by silica gel chromatography with chloroform/methanol affording 12 mg GA_{20}-ß-D-glucopyranosyl ester 9b (57 % yield, amorphous, ^{1}H-NMR see Tab. 2).

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