164. Glycosylidene Carbenes

Part 25[1])

Glycosidation of Ginkgolides B and A

by **Martin Weber** and **Andrea Vasella***

Laboratorium für Organische Chemie der ETH Zürich, Universitätstrasse 16, CH-8092 Zürich

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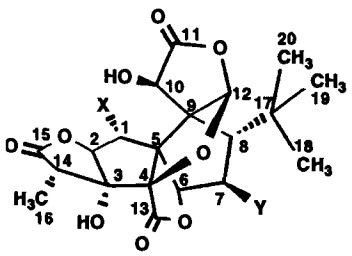
Ginkgolide B (**1b**) has been glucosylated in THF with the glucosylidene-derived diazirine **2** under thermal or photochemical conditions. Depending on the amount of **2**, we obtained either monoglucosides (**5**–**8**), diglucosides (**13**–**17**), or triglucosides (**21**–**23**). In keeping with earlier results, the use of THF as solvent led mostly to β-D-glucosides. The modest regioselectivity in the formation of the monoglucosides, glucosylated either at O–C(1) or O–C(10), is rationalized on the basis of the relative kinetic acidity of the intra- and intermolecularly H-bonded OH groups of **1b**. The tertiary HO–C(3) of the monoglucosides was more readily glucosylated than the secondary HO–C(1) or HO–C(10) (H-bonded). Glucosidation with 3.5 equiv. of **2** led to triglucosides, with the tri-β-D-glucoside **21** (42%) as the major product. Catalytic hydrogenation afforded the free glucosides **9**–**12**, **18**–**20**, and **24**. The di- and triglucosides are readily soluble in H_2O. Glucosidation with **2** of the ginkgolide-A-derived tertiary alcohol **25** yielded 93% of the β-D-anomeric glucoside **26**. Similarly, glycosidation of **25** with the lactosylidene-derived diazirine **34** proceeded with a very high stereoselectivity, yielding 92% of the β-D-lactoside **35**, that was deprotected to the H_2O soluble acetate **36**.

1. Introduction. – Ginkgolide B (**1b**) [2][3] is an antagonist (IC_{50} = 0.6 μM) [4] of the platelet activating factor (PAF[2]) [6]. It is not clear to which extent the weak solubility of **1b** in H_2O correlates with its bioavailability. Both might be improved by glycosidation. Ginkgolide B (**1b**) possesses a tertiary and two secondary OH groups. The poorly resolved X-ray structure of ginkgolide B monohydrate (**1b** · H_2O) [7] and of a solvate of ginkgolide C (**1c**) [8] is compatible with a H-bond between the secondary OH groups, possibly from HO–C(10) to HO–C(1). An intramolecular C(1)–OH···O–C(10) H-bond has been evidenced by the temperature dependence of the chemical shifts for a solution of ginkgolide B (**1b**) in DMSO [9]. The silylation of ginkgolide C (**1c**) with an excess of (*tert*-butyl)chlorodiphenylsilane and imidazole in DMF [10] led exclusively to the O–C(1) silyl ether, a result that is compatible with a C(1)–OH···O–C(10) H-bond. The weakly regioselective mono *O*-alkylation of HO–C(10) (benzyl chloromethyl ether or chloromethyl methyl ether, *Hünig*'s base) in MeCN, as reported by *Corey et al.* [11], has been related to the intervention of a H-bonded oxy anion.

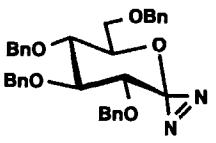
The regioselectivity of the glycosidation of diols and triols [12][13] by diazirine-derived glycosylidene carbenes is determined by the kinetic acidity of the individual OH

[1]) For part 24, see [1].

[2]) PAF is a potent bioregulator which appears to play a key role in acute allergy, inflammation, asthma, ischemic injury, and tissue rejection through its interaction with high affinity receptors ($EC_{50} \approx 10^{-10}$ M) [5].



Ginkgolide	X	Y	
A	H	H	**1a**
B	OH	H	**1b**
C	OH	OH	**1c**



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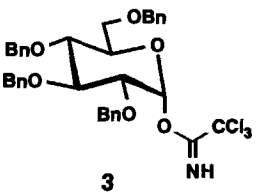

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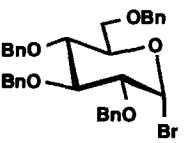

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groups and by the selectivity of interception of the ensuing oxycarbenium cation by an oxy anion or a OH group. Both processes are stereoelectronically controlled, protonation occurring in the σ-plane of the carbene and the nucleophilic attack in the π-plane of the oxycarbenium cation. The kinetic acidity of the OH groups depends most strongly on intra- and intermolecular H-bonds. Steric hindrance of sufficiently acidic OH groups is not a relevant factor in these glycosidations [14]; an excess of the glycosylidene-derived diazirine should allow glycosidation of the tertiary and of the secondary OH groups of **1b**.

2. Results and Discussion. – 1. *Glucosidation of Ginkgolide B* (**1b**). Glycosidations with glycosylidene-derived diazirines have been conducted under either photolytic or thermal conditions [13]. For glycosidations under photolytic conditions, the temperature ranged between -85 and $-15°$, while thermal conditions involved temperatures between 25 and 60°. Glycosidations have been carried out in 1,4-dioxane, THF, toluene, CH_2Cl_2, or $ClCH_2CH_2Cl$; of these, THF led to the highest anomeric selectivity, favoring β-D-anomers [15]. It also proved the only good solvent for ginkgolide B (**1b**).

In the ^{1}H-NMR spectrum of **1b** in (D_8)THF, HO–C(10) resonates at 6.78 ppm as d (J = 4.4 Hz), HO–C(3) at 5.44 ppm as s and HO–C(1) at 4.40 ppm as d (J = 3.4 Hz)[3]. Upon changing the solvent from THF to DMSO, the signals of HO–C(1) and HO–C(10) are shifted to lower field by a slightly different extent ($\Delta\delta$(HO–C(1)) = 0.49 and $\Delta\delta$(HO–C(10)) = 0.64 ppm, resp.), while the coupling constants were only weakly affected. This is in keeping with a H-bond from HO–C(1) to O–C(10), assuming that an intermolecular H-bond with the solvent is more strongly affected by the solvent change than an intramolecular H-bond. The value of the coupling constants J(1,OH) and J(10,OH) (*cf. Table 1*) are in keeping with this interpretation. The H-bonds of **1b** in solution ((D_8)THF) were characterized by the temperature dependence of the OH signals [16][17]. Similar dependencies were observed for HO–C(3) (the tertiary OH group) and HO–C(10) ($\Delta\delta/\Delta T = -5.0$ and -4.8 ppb/K, resp.), while the dependence for HO–C(1) was weaker ($\Delta\delta/\Delta T = -1.1$ ppb/K), similarly to the results in (D_6)DMSO [9].

We first investigated photolytic conditions for the generation of the glucosylidene carbene, as they enhance the anomeric selectivity of the glycosidation.

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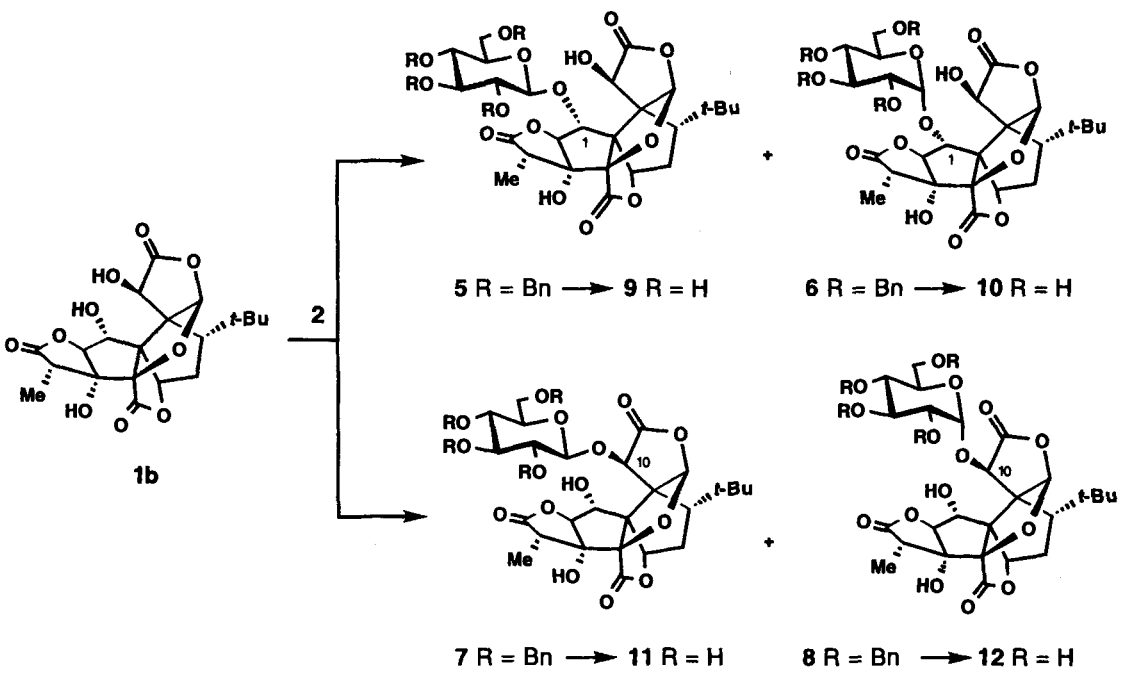
[3]) The assignment of the OH groups of **1b** is based on homonuclear decoupling and D_2O exchange experiments.

Irradiation (high-pressure Hg lamp) of a mixture of ginkgolide B (**1b**) and 1 equiv. of the diazirine **2** in THF at −70° led in 92% to a mixture of anomeric pairs of the regioisomeric monoglucosides **5**–**8** (**5**/**6**/**7**/**8** 51:8:30:11, *Scheme 1*). The tertiary HO–C(3) was at best glucosylated in trace amounts. As expected [15], the β-D-anomers dominated in both pairs of regioisomers (**5**/**6** 86:14; **7**/**8** 74:26). The ratio of the O–C(1) *vs.* O–C(10) monoglucosides ((**5** + **6**)/(**7** + **8**) 60:40), resulting from the glucosidation of **1b** in THF, is at first sight surprising. One expects protonation of the glucosylidene carbene by HO–C(10), the acceptor of the intramolecular H-bond and generation of the oxycarbenium cation in proximity of O–C(10). Glucosidation of HO–C(10) *and* HO–C(1) then requires a conformation of the C(10)–OH group, implying a sharp H···O–H angle, for which there is no evidence and little precedent in the absence of a second intramolecular H-bond acceptor [12e]. Generation of the oxycarbenium cation in proximity to HO–C(1) and HO–C(10) would also result from deprotonation of the intramolecular H-bond donor HO–C(1). This would require that the intermolecular H-bond be stronger than the intramolecular H-bond. Deprotection of **5**–**8** yielded **9**–**12**, respectively (see below).

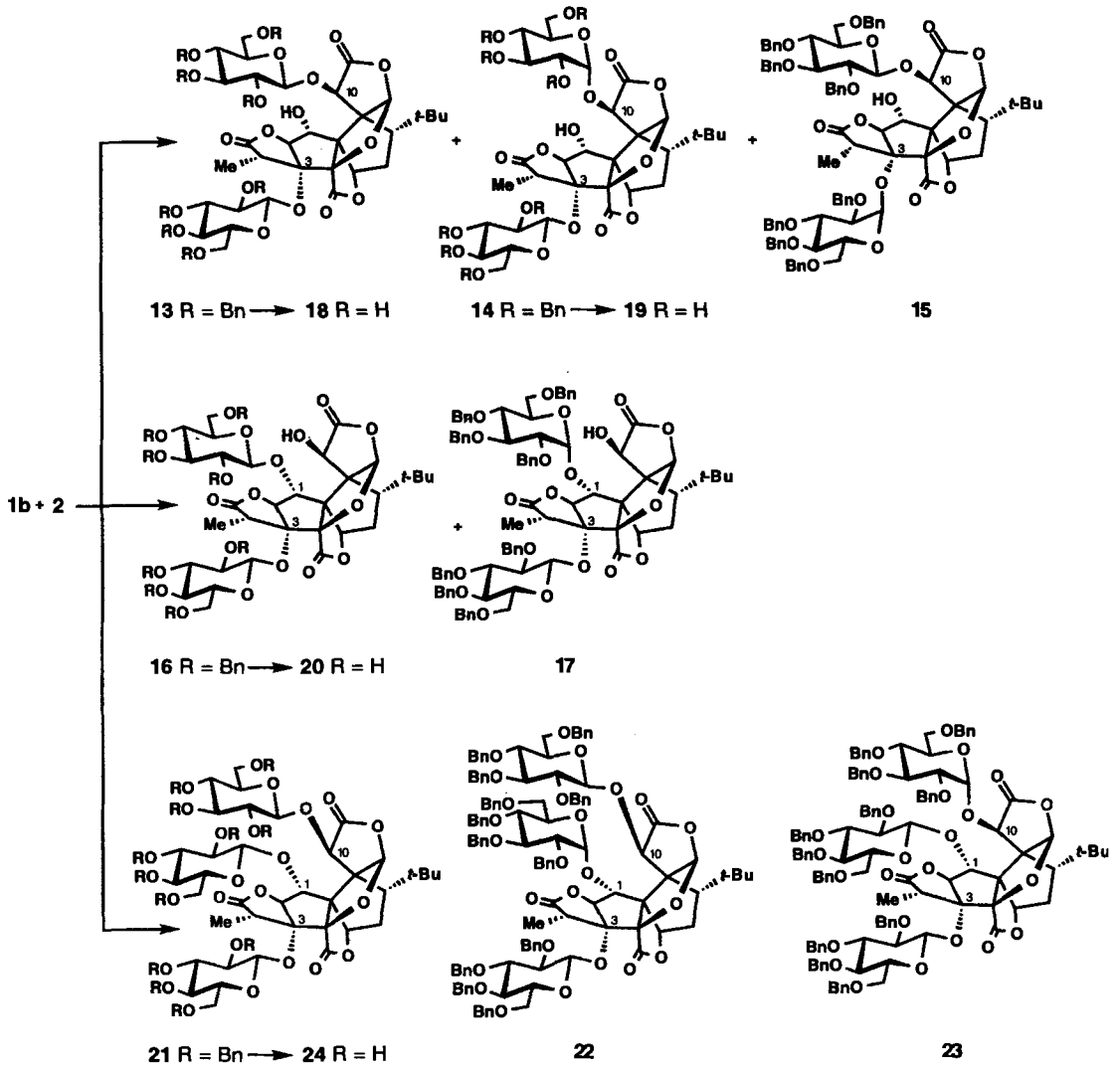
Scheme 1



Similar glycosidations of **1b**, but with 1.5–3 equiv. of **2**, led to slightly lower yields (87–91%) of the monoglucosides **5**–**8**, small amounts (3–8%) of the diglucosides **13** and **16** (*Scheme 2, cf.* below), and increasing amounts (11–32%) of by-products derived from **2**, such as lactone azines [18] and 3,4,6-tri-*O*-benzyl-2-(benzyloxy)-D-glucal [18][19].

Glucosidation of **1b** in THF under thermal conditions (25°) with 1 equiv. of **2** led to the monoglucosides **5**–**8** in yields between 43 and 64%[4]). We also isolated small amounts of the diglucosides **13** (4%), **14** (3%), and **16** (2%; *Scheme 2*), and the triglucoside **21** (1%, *cf.* below). This should be compared to the reaction of **1b** with 3.5 equiv. of benzyl chloromethyl ether or 5 equiv. of chloromethyl methyl ether in the presence of 4–5 equiv. of *Hünig*'s base, where only monoacetals were formed [11].

Scheme 2



[4]) Under similar conditions, glucosidations in 1,4-dioxane, toluene, CH_2Cl_2, or $CHCl_3$ with 1 equiv. of **2** led to a mixture of **5**–**8** in yields reaching 30%, in the best case.

Glucosidation of **1b** in THF at 30° with 2 equiv. of **2** (added in sequence) yielded 45% of the monoglucosides **5**, **7**, and **8**, and, in accordance with the low influence of steric hindrance in the glucosidation with the diazirine **2**[5]), 26% of the diglucosides **13**–**17**, and 4% of the triglucosides **21**–**23** (*Scheme 2*). The 1,10-di-*O*-glucosylated products were not obtained. The ratio of the isolated monoglucosides **5**/**7**/**8** was 27:37:36. Of the expected eight diglucosides (four anomeric pairs of regioisomers glucosylated at O–C(10)/O–C(3), or O–C(1)/O–C(3)), only five were isolated in the ratio **13**/**14**/**15**/**16**/**17** of 39:25:7:19:10, and, of these five diglucosides, only one isomer (**15**) was α-D-glucosylated at O–C(3). The ratio of the anomeric pair **13** and **15** was 85:15 (β-D/α-D)[6])[7]). Under these conditions, the ratio of the three isolated triglucosides **21**/**22**/**23** was 44:27:29. None of these three triglucosides was α-D-glucosylated at O–C(3), and none possessed more than one α-D-glucosyl moiety. Deprotection of **13**, **14**, **16**, and **21** yielded **18**–**20** and **24**, respectively (see below).

The constitution of the diglucosides shows that, after one of the secondary HO–C(1) or HO–C(10) has been glucosylated, the tertiary HO–C(3) of **5**–**8** is more readily glucosylated than the remaining secondary HO; this is in keeping with the presumption that HO–C(1) in **7** and **8**, or HO–C(10) in **5** and **6**, forms a H-bond, as evidenced in the case of **5** and **6** (*cf.* below). However, as shown by the formation of triglucosides, even the H-bonded HO–C(1) or HO–C(10) of the diglucosides reacted with **2** (*cf.* [13h][14]).

Glucosidation of **1b** in THF at 25° with two times 2 equiv. of **2** yielded 24% of the α-D,β-D-diglucosylated **14**, and 70% of the triglucosides **21**, **22**, and **23**, in a ratio of 59:22:19. As expected, the main product was the tri-β-D-glucoside **21**, isolated in a yield of 42%.

In our hands, the glucosidation of ginkgolide B (**1b**) with 1.25 equiv. of the trichloroacetimidate **3** in the presence of $BF_3 \cdot OEt_2$, or trimethylsilyl triflate at 0–40°, or with 1.0 to 4.0 equiv. of the glycosyl bromide **4** and Et_4NBr as promoter at 25–50° in THF was not successful.

Debenzylation of **5**–**8**, **13**, **14**, **16**, and **21** by catalytic hydrogenation led in 90–98% to the corresponding glucosides **9**–**12**, **18**–**20**, and **24**, respectively. The monoglucosides **9**–**12** are poorly soluble in H_2O, while the diglucosides **18**–**20** and the triglucoside **24** are freely H_2O-soluble.

2. *Glucosidation of Ginkgolide A* (**1a**). The results of the glucosidation of ginkgolide B (**1b**) shows an exceptionally high diastereoselectivity for the glucosidation at HO–C(3). Glycosidation of a ginkgolide, possessing only this tertiary OH group should, therefore, lead in high yields to a single glycoside. Thus, ginkgolide A (**1a**) was acetylated at HO–C(10) [20]. The monoacetate **25** was glucosylated in THF with 1.3 equiv. of **2** (*Scheme 3*). The ^{1}H-NMR spectrum of the crude product showed a ratio of 97:3 for the β-D-glucoside **26** and its α-D-anomer. Crystallization gave 85% of **26**; chromatography

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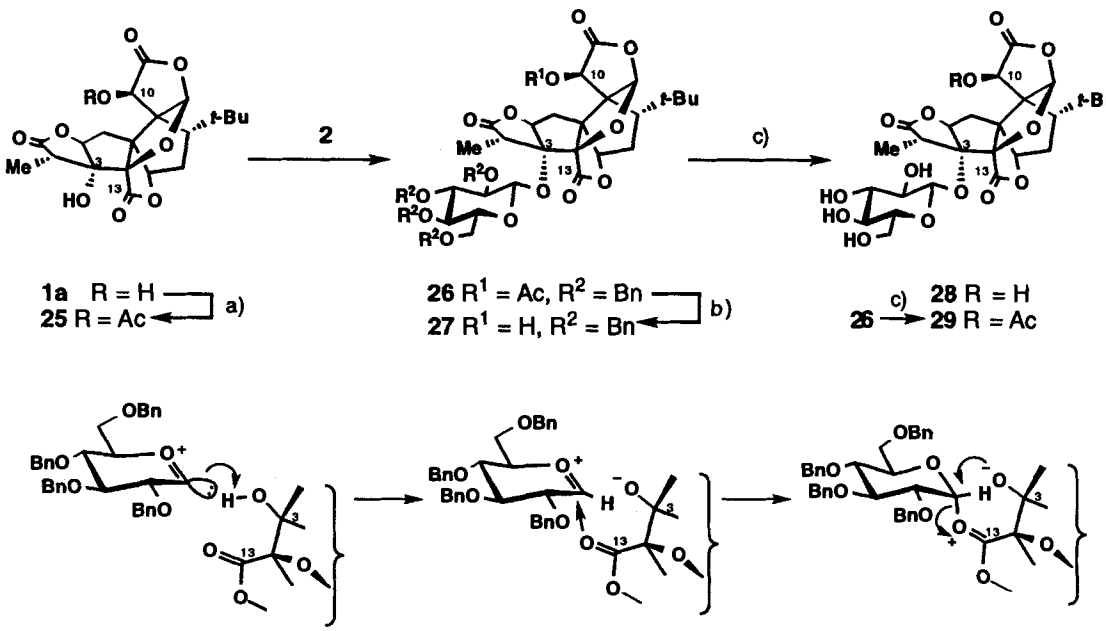
[5]) The low influence of steric hindrance during the glycosidation of phenols with glycosylidene diazirines has been shown before [14].

[6]) This ratio cannot be used to describe the diastereoselectivity of the glucosidation of HO–C(3), since **13** is partially consumed under the reaction conditions to give the triglucosides **21** and **22**.

[7]) One expects a maximum yield of 0.5–1.1% for the formation of the diastereoisomers of **14**, **16**, and **17**, α-D-glucosylated at O–C(3), if the glucosidation proceeded with the same ratio as given for the isomers **13** and **15**.

of the mother liquor increased the total yield of **26** to 93%. The high diastereoselectivity is explained in the framework of the detailed reaction mechanism that has been proposed before [15]. Briefly, the OH group is deprotonated by the carbene to generate an ion pair, where the oxy anion is in the σ-plane of the oxycarbenium cation. For this reason, the cation is stabilized either by solvation or by neighboring group participation before it can be attacked by the oxy anion. In either case, the preferential interaction of the nucleophilic ligand from the axial side leads to equatorial glucosides. In the glucosidation of the secondary OH groups of **5**–**8**, the oxycarbenium cation is solvated by THF; in the glycosidation of the tertiary HO–C(3), neighboring group participation by the C(13) carbonyl function ensures a particularly effective solvation and, hence, a high diastereoselectivity of the glycosidation (*cf. Scheme 3*).

Scheme 3

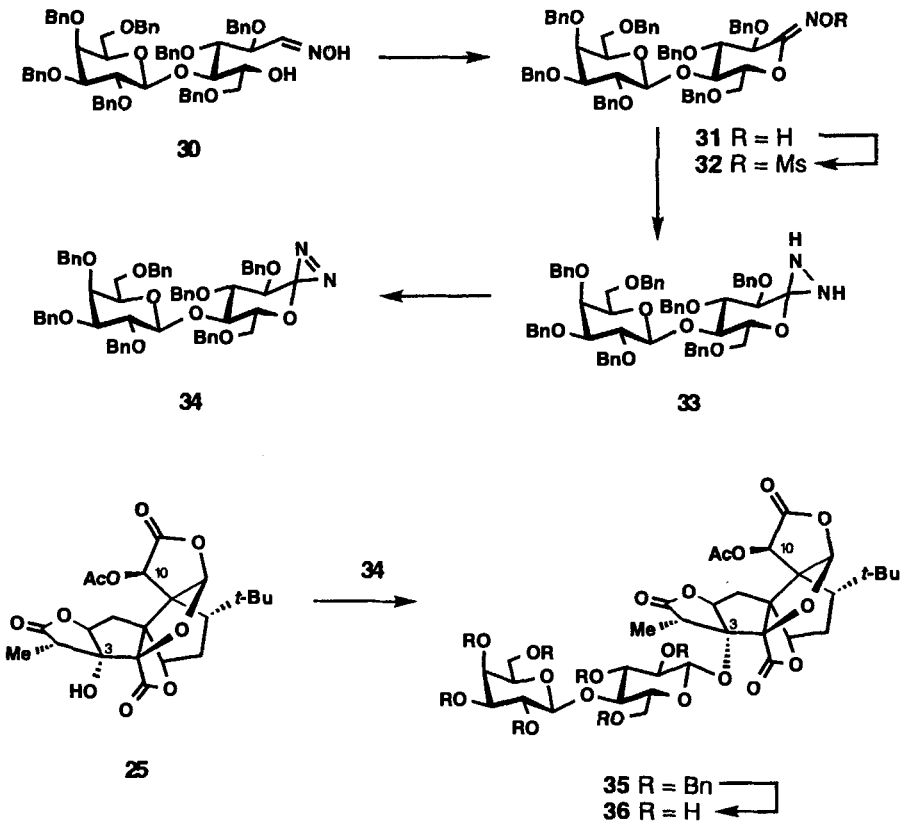


a) Ac_2O, py. b) NH_3, MeOH. c) Pd/C, 10%, H_2.

Deacetylation of **26** proved difficult. A range of acidic or basic conditions resulted in poor yields of **27**, and the best yields, obtained by treating **26** with NH_3 in MeOH/CH_2Cl_2, did not exceed 46%. Catalytic debenzylation of **27** gave 84% of **28**. The converse sequence, *i.e.*, debenzylation of **26** to **29**, followed by deacetylation to **28**, was even less satisfactory, although the catalytic debenzylation of **26** proceeded in 98% yield.

As the glucoside **28** proved only weakly soluble in H_2O, we glycosylated **25** with the lactosylidene-derived diazirine **34** (*Scheme 4*). This diazirine was synthesized from 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactosyl)-D-glucopyranose [21] following the established method [18][22]. The oxime **30** was obtained as (*E*/*Z*)-mixture (70:30, 94%) and oxidized with MnO_2 [23] to the (*Z*)-hydroximolactone **31** (87%). Mesylation (→ **32**, 99%), followed by treating **32** with NH_3 in MeOH yielded 90% of the diaziridine

Scheme 4



33. It proved to be a 98:2 mixture of the two *trans*-diastereoisomers, as evidenced by the two sets of signals for the hydrazi group in the ^{1}H-NMR spectra (*cf.* [18]). The diazirine **34** was prepared by oxidizing **33** with I_2 in CH_2Cl_2. Rapid filtration through silica gel gave **34** (97%) as a colorless foam. It had a half-life $\tau_{1/2}$ at 25° of 85 min, higher than **2** ($\tau_{1/2}$ = 33 min [18]), and kept well for months at −78° in solution (THF or CH_2Cl_2), or in the solid state.

Glycosidation of **25** in THF with 1.1 equiv. of **34** yielded 92% of the β-D-lactoside **35**. The α-D-anomer was at best formed in trace amounts; it was neither observed in the ^{1}H-NMR spectrum of the crude product, nor detected by prep. HPLC. Catalytic debenzylation of **35** led in 99% to the O–C(10) acetylated β-D-lactoside **36**. It is freely H_2O-soluble.

The constitution of the monoglucosylated regioisomers **5**–**8** was assigned on the basis of the coupling pattern of H–C(1) (*dd*) and H–C(10) (*d*), and by D_2O exchange experiments (change of the coupling pattern *dd* → *d*, *d* → *s* of H–C(1) and H–C(10); the signal for HO–C(3) disappears). The diastereoisomers **5** and **6** as well as **7** and **8** were differentiated by the chemical shift and coupling constant of H–C(1') (*Table 1*). The position of the glucosyl residues in the diglucosides **13**–**17** was assigned on the basis of the multiplicity and the chemical shift of H–C(1) and H–C(10), and the characteristic chemical shift to lower field of the anomeric proton of the α-D-glucosyl moiety attached at O–C(10) (*Table 1*). This chemical shift was also used to differentiate between the

Table 1. *Selected ^{1}H-NMR* (500 MHz, (D_6)acetone) *Data of Ginkgolide B* (**1b**) *and the Glucosides* **5**–**24**[a]). Chemical shifts δ in [ppm], coupling constants J in [Hz].

	H–C(1)	HO–C(1)	H–C(2)	H–C(10)	HO–C(10)	H–C(1′)	H–C(1″)	H–C(1‴)	*J*(1,OH)	*J*(1,2)	*J*(10,OH)	*J*(1′,2′)	*J*(1″,2″)	*J*(1‴,2‴)
1b	4.25	4.35	4.67	5.31	6.73				3.1	7.9	4.9			
5	[c])		[c])	5.21	5.89[d])	4.75				[c])	4.4	7.7		
6[e])	4.62		[c])	5.18[f])	5.68[d])	5.35				5.6	4.5	3.7		
7	4.40[g])	4.64[d])	4.65	5.53		5.29			5.4	7.5		7.5		
8[e])	4.35[g])	5.32[d])	4.53	5.57		6.25			6.5	7.6		4.5		
9[e])	4.44		4.93	5.26		4.53				5.5		7.8		
10[i])	4.71		4.82	5.05		5.11				4.0		3.7		
11	4.27[g])	4.96[d])	4.59	5.73		4.88				7.4		7.5		
12[i])	4.29		4.52	5.38		6.15				7.5		3.7		
13	4.47[g])	4.8–4.6[h])	5.22	5.51		5.27	4.8–4.6[h])		5.6	7.2		7.5	7.8[j])	
14	4.44[g])	5.47[f])	5.07	5.59		6.26	4.8–4.5[h])		6.5	6.8		4.1	7.5	
15	4.33[g])	3.97[d])	5.22	5.14		4.9–4.7[h])	4.50		3.4	7.5		7.8	4.2[j])	
16	4.45		5.48	5.28[f])	5.97[d])	4.81	4.65			5.6	5.0	7.5	7.5	
17	4.7–4.5[h])		5.28	5.18[f])	5.57[d])	5.36	4.45			5.6	4.4	3.7	7.5	
18	4.30		5.25	5.65		4.73	4.49			7.2		7.2	7.5	
19[i])	4.36		5.22	5.39		6.14	4.49			7.5		4.1	7.5[j])	
20[i])	4.42		5.59	5.12		4.38	4.49			5.3		7.5	7.8	
21[b])	4.83		5.61	5.50		5.34	5.01	4.82		3.4		7.9	7.8	8.1
22	5.18		5.30	5.40		5.84	5.06	4.97		2.7		4.3	7.9	7.9
23	5.31		5.65	5.46		6.19	5.38	5.20		[c])		4.5	7.9	7.6
24[i])	4.77		5.64	5.44		4.76	4.74	4.67		1.9[k])		7.5	7.8	7.8

[a]) For other data see *Exper Part.* [b]) At 300 MHz. [c]) Not assigned. [d]) Exchanged with D_2O. [e]) At 400 MHz. [f]) Addition of $D_2O \rightarrow s$. [g]) Addition of $D_2O \rightarrow d$. [h]) Hidden by other signals. [i]) Measured in CD_3OD at 300 MHz. [j]) Determined from the signal of H–C(2″). [k]) Determined from the signal of H–C(2).

Table 2. *Selected* ^{13}C*-NMR Signals of the Glucosides* **1b**, **5**–**12**, **18**, **20**, *and* **24**. Chemical Shifts δ in [ppm][a]).

	1b	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**18**	**20**	**24**
C(1)	75.4	83.7[b])	82.3	75.2[b])	73.7[b])	83.2	81.1	72.7[b])	74.8[b])	73.5[b])	84.5	85.6
C(2)	92.5	95.5	93.7[b])	93.5	93.3[c])	94.0	94.2	93.3	94.7[c])	88.1	88.9	91.5
C(3)	84.8	86.2	85.4	83.9	83.4	85.5	85.8	84.1	83.1	90.0	91.3	92.2
C(6)	80.0	80.2	79.8[c])	79.5	79.2[d])	80.1	80.3	79.4	80.4	80.3	81.0	80.6
C(10)	70.8	70.4	70.1	75.9[b])	74.7[b])	70.4	71.0	75.5[b])	74.8[b])	75.5[b])	70.0	75.3[b])
C(1')[f])		104.0	96.3[b])			103.8	98.7				104.5	105.5
C(2')		83.4[b])	80.1[c])			75.0	73.3[b])				75.3[c])	74.7[b])
C(3')		85.8[b])	81.1			77.8	74.7				77.9[b])	78.1[c])
C(4')		79.8	78.9			71.5	70.4				71.2[d])	71.8[d])
C(5')		76.0	72.5			77.9	74.2[b])				77.8[b])	78.2[c])
C(6')		69.7	69.8			62.8	61.9				62.4	62.9[e])
C(1'')[g])				100.5	96.6[c])			99.8	98.3[c])	100.6		105.5
C(2'')				81.6	80.8[d])			75.6[b])	72.4[b])	76.6[b])		77.7[c])
C(3'')				85.9	81.8			77.7[b])	74.1[b])	77.8[b])		77.9[c])
C(4'')				78.7[b])	77.9			71.6	70.2	71.4		71.5[d])
C(5'')				74.9[b])	73.7[b])			78.7[b])	73.5[b])	79.2		78.9[e])
C(6'')				69.4	69.1			62.6	61.5	62.6		62.8[e])
C(1''')[h])										99.5	99.8	100.4
C(2''')										74.6[b])	74.6[c])	74.4[b])
C(3''')										77.9[b]	78.0[b])	78.0[c])
C(4''')										70.9	71.1[d])	70.9[d])
C(5''')										78.6	78.5[b])	78.5[c])
C(6''')										62.3	62.4	61.9[e])

[a]) For other signals see *Exper. Part.* [b])[c])[d])[e]) Assignment may be interchanged. [f]) ' for the glucosyl residue at O–C(1). [g]) '' for the glucosyl residue at O–C(10). [h]) ''' for the glucosyl residue at O–C(3).

triglucosides **22** and its anomer **23** (*Table 1*). In the ^{13}C-NMR spectra of the glucosides **5**–**12**, **18**, **20**, and **24**, the position of the glucosyl residues is also indicated by the downfield shift of the signals for C(1), C(3), and C(10), respectively (*Table 2*).

Upon glucosidation at O–C(1), the conformational equilibrium of the ring A for the mono- and diglucosides **5**, **6**, **9**, **10**, **16**, **17**, and **20** is shifted from $^2T_1$ to an equilibrium $^2T_1/^3T_4$ *ca.* 2:1 (derived from $J(1,2)$ in *Table 1*), presumably due to the ability of a H-bond from HO–C(10) to O–C(1). Glucosidation of HO–C(10) does not affect the equilibrium of the ring A. The triglucosides **21**–**23** appear to exist predominately in the $^3T_4$ conformation. These results are in keeping with a preferred direction of the H-bond from HO–C(1) to O–C(10).

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Experimental Part

1. *General.* ^1H-NMR spectroscopy ((D_8)THF) showed that the sample of ginkgolide B (**1b**) contains at the best only traces of H_2O. A suspension of **1b** in toluene was concentrated to dryness *i.v.* several times before use. Glucosidations were run under Ar in dry THF. TLC: *Merck* silica gel *60* F_{254} plates; detection by heating at 400° and treating with a soln. of 5% $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and 0.1% $Ce(SO_4)_2 \cdot 4H_2O$ in 10% H_2SO_4. Flash chromatography (FC): silica gel (*Fluka* or *Merck 60*; 0.040–0.063 mm). HPLC: *Spherisorb*® SiO_2 (5 μm) column (20 × 250 mm); detection at 254 nm; t_R in min. IR spectra: $CHCl_3$ was filtered through a column of activated alumina. NMR spectra: chemical shifts δ in ppm and coupling constants J in Hz.

2. *Treatment of Ginkgolide B* (**1b**) *with 1 equiv. of* **2**. A soln. of **1b** (134 mg, 0.31 mmol) in THF (4 ml) was cooled to −75°, treated with a soln. of **2** (177 mg, 0.32 mmol) in THF (1.5 ml), and irradiated (*Philips HPK-125* high-pressure Hg lamp) for 1 h at −70°. The mixture was warmed to 23° and evaporated. Filtration through SiO_2

(AcOEt) and HPLC (hexane/AcOEt 2:1; 6 ml/min) gave **7** (82.4 mg, 27%; t_R 18.2), **6** (23 mg, 8%; t_R 19.5), **8** (29.8 mg, 10%; t_R 20.2), and **5** (140.3 mg, 47%; t_R 24.0).

1-O-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)ginkgolide B (**5**): IR ($CHCl_3$): 3564*w*, 3451*w*, 3328*w*, 3090*w*, 3066*w*, 3007*m*, 2966*m*, 2913*m*, 2873*m*, 1952*w*, 1794*s*, 1604*w*, 1497*w*, 1454*m*, 1405*m*, 1360*m*, 1324*m*, 1310*m*, 1172*m*, 1143*s*, 1070*s*, 1028*s*, 962*m*, 906*m*. ^{1}H-NMR (500 MHz, (D_6)acetone, assignment based on H,H–*COSY*): *Table 1*; 7.42–7.24 (*m*, 20 arom. H); 6.02 (*s*, H–C(12)); 5.60 (*d*, J = 3.7, H–C(6)); 5.50 (*s*, exchange with D_2O, HO–C(3)); 4.98–4.96 (*m*, 2 H); 4.87 (*d*, J = 11.2, PhC*H*); 4.84–4.79 (*m*, 3 H); 4.76 (*d*, J = 11.3), 4.67 (*d*, J = 11.1), 4.66 (*d*, J = 12.3), 4.60 (*d*, J = 12.3, 4 PhC*H*); 3.83 (*dd*, J = 2.0, 11.0, H–C(6′)); 3.78 (*dd*, J = 3.9, 11.0, H′–C(6′)); 3.71 (*t*, J = 8.9, H–C(4′)); 3.66 (*t*, J = 8.5, H–C(3′)); 3.51 (*ddd*, J = 1.9, 3.9, 9.5, H–C(5′)); 3.46 (*t*, J = 8.1, H–C(2′)); 3.06 (*q*, J = 7.5, H–C(14)); 2.10 (*dt*, J = 3.9, 13.8, H–C(7)); 2.03 (*dd*, J = 4.7, 13.5, H′–C(7)); 1.93 (*dd*, J = 4.7, 14.0, H–C(8)); 1.29 (*d*, J = 7.5, Me–C(14)); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz, (D_6)acetone): *Table 2*; 176.5 (*s*); 173.9 (*s*); 171.7 (*s*); 140.1 (*s*); 139.9 (*s*); 139.8 (*s*); 139.8 (*s*); 129.3–128.4 (several *d*) 110.1 (*d*); 103.3 (*s*); 76.1 (*t*); 75.4 (2*t*); 74.9 (*s*); 74.2 (*t*); 70.2 (*s*); 50.6 (*d*); 42.1 (*d*); 37.8 (*t*); 33.3 (*s*); 10.4 (*q*); (*q*, Me_3C hidden by acetone). FAB-MS: 1892 (3, $2M^+$), 969 (64, $[M + Na]^+$), 947 (32, $[M + H]^+$), 946 (65, M^+), 945 (100), 855 (19), 515 (69), 425 (38), 271 (28), 181 (87), 91 (100).

1-O-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl)ginkgolide B (**6**): IR ($CHCl_3$): 3566*w*, 3342*w*, 3089*w*, 3069*w*, 3007*m*, 2966*m*, 2873*m*, 1795*s*, 1603*w*, 1497*w*, 1454*m*, 1406*w*, 1357*m*, 1326*m*, 1284*w*, 1168*s*, 1100*s*, 1068*s*, 1029*s*, 986*m*, 962*m*, 902*m*. ^{1}H-NMR (400 MHz, (D_6)acetone): *Table 1*; 7.34–7.18 (20 arom. H); 6.08 (*s*, H–C(12)); 5.62 (*d*, J = 3.5, H-C(6)); 5.36 (*s*, exchange with D_2O, HO–C(3)); 4.93 (*d*, J = 11.2, PhC*H*); 4.87–4.81 (*m*, 5 H); 4.79 (*d*, J = 11.6), 4.60 (*d*, J = 12.2), 4.57 (*d*, J = 12.1, 3 PhC*H*); 4.21 (*dt*, J = 3.0, 10.1, H–C(5′)); 3.90 (*t*, J = 9.4, H–C(3′)); 3.70 (br. *d*, J = 3.1, 2 H–C(6′)); 3.61 (*dd*, J = 3.7, 9.6, H–C(2′)); 3.57 (*dd*, J = 9.1, 10.1, H–C(4′)); 3.12 (*q*, J = 7.2, H–C(14)); 2.20 (*dd*, J = 5.2, 13.4, H–C(7)); 2.19–2.13 (*m*, H′–C(7)); 1.92 (*dd*, J = 5.2, 13.5, H–C(8)); 1.28 (*d*, J = 7.2, Me–C(14)); 1.14 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, (D_6)acetone): *Table 2*; 176.2 (*s*); 173.9 (*s*); 171.1 (*s*); 140.1 (*s*); 139.7 (*s*); 139.5 (2*s*); 129.2–128.2 (several *d*); 110.5 (*d*); 101.0 (*s*); 75.7 (2*t*); 73.9 (2*t*); 73.6 (*s*); 69.8 (*s*); 50.0 (*d*); 42.5 (*d*); 37.6 (*t*); 33.1 (*s*); 8.8 (*q*); (*q*, Me_3C hidden by acetone).

10-O-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)ginkgolide B (**7**): IR ($CHCl_3$): 3565*m*, 3490*m*, 3090*w*, 3067*m*, 3008*m*, 2966*m*, 2944*m*, 2915*m*, 2872*m*, 1951*w*, 1785*s*, 1605*w*, 1497*m*, 1454*s*, 1406*m*, 1361*s*, 1327*m*, 1314*m*, 1280*m*, 1163*s*, 1098*s*, 1028*s*, 988*s*, 967*s*, 926*m*. ^{1}H-NMR (500 MHz, (D_6)acetone; assignment based on H,H–*COSY*): *Table 1*; 7.51–7.08 (*m*, 20 arom. H); 6.12 (*s*, H–C(12)); 5.36–5.35 (*m*, H–C(6)); 5.28 (*s*, exchange with D_2O, HO–C(3)); 5.04 (*d*, J = 11.8), 4.92 (*d*, J = 11.2), 4.81 (*d*, J = 10.3), 4.80 (*d*, J = 11.7), 4.79 (*d*, J = 11.0), 4.70 (*d*, J = 11.0), 4.69 (*d*, J = 12.0), 4.57 (*d*, J = 12.0, 8 PhC*H*); 3.87 (*t*, J = 8.6, H–C(3′)); 3.83 (*dd*, J = 3.9, 11.2, H–C(6′)); 3.80 (*t*, J = 8.7, H–C(4′)); 3.71 (*dd*, J = 2.0, 11.5, H′–C(6′)); 3.70–3.67 (*m*, H–C(5′)); 3.64 (*dd*, J = 7.5, 8.4, H–C(2′)); 3.09 (*q*, J = 7.0, H–C(14)); 2.05–1.96 (*m*, H–C(7), H–C(8)); 1.86–1.82 (*m*, H′–C(7)); 1.28 (*d*, J = 7.0, Me–C(14)); 1.06 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz, (D_6)acetone): *Table 2*; 176.8 (*s*); 171.0 (*s*); 170.3 (*s*); 139.6 (*s*); 139.4 (3*s*); 129.3–127.9 (several *d*); 110.3 (*d*); 99.7 (*s*); 75.6 (*t*); 75.3 (*t*); 74.4 (*t*); 74.2 (*t*); 73.3 (*s*); 69.0 (*s*); 50.1 (*d*); 42.9 (*d*); 37.6 (*t*); 32.8 (*s*); 8.2 (*q*); (*q*, Me_3C hidden by acetone).

10-O-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl)ginkgolide B (**8**): IR ($CHCl_3$): 3566*w*, 3388*m*, 3090*w*, 3067*w*, 3008*m*, 2964*m*, 2916*m*, 2874*m*, 1952*w*, 1790*s*, 1604*w*, 1497*w*, 1454*m*, 1406*w*, 1363*m*, 1326*m*, 1312*m*, 1165*s*, 1103*s*, 1069*s*, 1028*s*, 1005*m*, 987*s*, 966*m*, 920*m*. ^{1}H-NMR (400 MHz, (D_6)acetone, assignment based on H,H–*COSY*): *Table 1*; 7.39–7.06 (20 arom. H); 6.25 (*s*, H–C(12)); 5.42 (br. *d*, J = 3.9, H–C(6)); 5.31 (*s*, exchange with D_2O, HO–C(3)); 5.07 (*d*, J = 10.8), 4.83 (*d*, J = 10.7), 4.81 (*d*, J = 11.0), 4.77 (*d*, J = 11.2), 4.75 (*d*, J = 11.3), 4.62 (*d*, J = 10.7), 4.60 (*d*, J = 11.9), 4.52 (*d*, J = 11.9, 8 PhC*H*); 3.88–3.70 (*m*, 5 H); 3.55 (*dd*, J = 1.4, 10.7, H′–C(6′)); 3.07 (*q*, J = 7.0, H–C(14)); 2.24 (*dd*, J = 4.3, 13.4, H–C(7)); 2.04–1.96 (*m*, H′–C(7)); 1.85 (*dd*, J = 4.1, 14.5, H–C(8)); 1.28 (*d*, J = 7.0, Me–C(14)); 1.18 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, (D_6)acetone): *Table 2*; 176.6 (*s*); 172.9 (*s*); 171.0 (*s*); 139.6 (*s*); 139.5 (*s*); 139.4 (*s*); 137.6 (*s*); 129.4–128.3 (several *d*); 110.7 (*d*); 99.6 (*s*); 76.1 (*t*); 75.8 (*t*); 75.7 (*t*); 74.1 (*t*); 72.9 (*s*); 69.2 (*s*); 49.6 (*d*); 42.9 (*d*); 38.4 (*t*); 33.1 (*s*); 8.2 (*q*); (*q*, Me_3C hidden by acetone).

3. *Debenzylations:* **9**–**12**. *1-O-(β-D-Glucopyranosyl)ginkgolide B* (**9**). A mixture of **5** (73.0 mg, 0.077 mmol) and 10% Pd/C (100 mg) in MeOH (3.0 ml) was hydrogenated at 3.5 atm for 17 h. Filtration and evaporation gave **9** (42.7 mg, 94%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.37. ^{1}H-NMR (400 MHz, (D_6)acetone; assignment based on H,H-*COSY*): *Table 1*; 6.09 (*s*, H–C(12)); 5.55–5.35 (*m*, H–C(6)); 3.85–3.79 (*m*, H–C(6′)); 3.66 (*dd*, J = 5.4, 11.6, H′–C(6′)); 3.47 (*t*, J = 8.8, H–C(3′)); 3.40–3.33 (*m*, H–C(4′), H–C(5′)); 3.28 (*dd*, J = 7.8, 8.9, H–C(2′)); 3.09 (*q*, J = 7.2, H–C(14)); 2.25–2.18 (*m*, 2 H–C(7)); 1.94 (*dd*, J = 6.5, 12.4, H–C(8)); 1.25 (*d*, J = 7.4, Me–C(14)); 1.26 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, (D_6)acetone): *Table 2*; 176.4 (*s*); 173.9 (*s*); 170.9 (*s*); 110.6 (*d*); 100.8 (*s*); 73.2 (*s*); 69.6 (*s*); 50.0 (*d*); 42.4 (*d*); 37.7 (*t*); 33.1 (*s*); 31.9 (3*q*); 8.8 (*q*).

1-O-(α-D-Glucopyranosyl)ginkgolide B (**10**). A mixture of **6** (20.1 mg, 0.021 mmol) and 10% Pd/C (50 mg) in MeOH (3.0 ml) was hydrogenated at 2.1 atm for 17 h. Filtration and evaporation gave **10** (6.5 mg, 52%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.41. ^{1}H-NMR (300 MHz, CD_3OD): *Table 1*; 6.00 (*s*, H–C(12)); 5.67 (br. *d*, *J* = 3.1, H–C(6)); 3.90 (*ddd*, *J* = 2.6, 3.4, 9.6, H–C(5′)); 3.81 (*dd*, *J* = 2.5, 12.1, H–C(6′)); 3.73 (*dd*, *J* = 3.7, 11.8, H′–C(6′)); 3.61 (*dd*, *J* = 9.0, 9.9, H–C(3′)); 3.47 (*dd*, *J* = 3.7, 9.9, irrad. at 5.11 → *d*, *J* = 9.7, H–C(2′)); 3.44 (*dd*, *J* = 9.0, 9.9, H–C(4′)); 3.07 (*q*, *J* = 7.2, H–C(14)); 2.22–2.10 (*m*, 2 H–C(7)); 1.89 (*dd*, *J* = 5.6, 12.5, H–C(8)); 1.24 (*d*, *J* = 7.5, Me–C(14)); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, CD_3OD): *Table 2*; 178.1 (*s*); 175.2 (*s*); 173.1 (*s*); 110.8 (*d*); 103.2 (*s*); 74.9 (*s*); 70.6 (*s*); 50.8 (*d*); 42.8 (*d*); 37.8 (*t*); 33.4 (*s*); 29.6 (3*q*); 9.6 (*q*).

10-O-(β-D-Glucopyranosyl)ginkgolide B (**11**). A mixture of **7** (32.0 mg, 0.034 mmol) and 10% Pd/C (100 mg) in MeOH (3.0 ml) was hydrogenated at 3.5 atm for 17 h. Filtration, evaporation and FC (750 mg of SiO_2, AcOEt/MeOH/H_2O 8.5:1.5:1) gave **11** (19.8 mg, 88%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.43. ^{1}H-NMR (500 MHz, (D_6)acetone; assignment based on H,H-*COSY*): *Table 1*; 6.15 (*s*, H–C(12)); 5.43 (*d*, *J* = 4.0, H–C(6)); 5.27 (br. *s*, exchange with D_2O, HO–C(3)); 3.87–3.83 (*m*, H–C(6′)); 3.78 (*m*, H′–C(6′)); 3.66–3.62 (*m*, H–C(5′)); 3.49–3.45 (*m*, H–C(2′)); 3.41–3.34 (*m*, H–C(3′), H–C(4′)); 3.02 (*q*, *J* = 7.1, H–C(14)); 2.28 (*dd*, *J* = 4.3, 13.5, H–C(7)); 2.08–2.01 (*m*, H′–C(7)); 1.93 (*dd*, *J* = 4.3, 14.6, H–C(8)); 1.26 (*d*, *J* = 7.1, Me–C(14)); 1.21 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz, (D_6)acetone): *Table 2*; 176.7 (*s*); 171.6 (*s*); 171.1 (*s*); 110.0 (*d*); 99.8 (*s*); 73.6 (*s*); 69.2 (*s*); 50.5 (*d*); 43.0 (*d*); 37.7 (*t*); 32.9 (*s*); 29.7 (3*q*); 8.2 (*q*).

10-O-(α-D-Glucopyranosyl)ginkgolide B (**12**). A mixture of **8** (45.1 mg, 0.048 mmol) and 10% Pd/C (50 mg) in MeOH (3.0 ml) was hydrogenated at 2.1 atm for 17 h. Filtration and evaporation gave **12** (27.5 mg, 98%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.50. ^{1}H-NMR (300 MHz, CD_3OD): *Table 1*; 6.14 (*s*, H–C(12)); 5.44 (*d*, *J* = 4.0, H–C(6)); 3.79–3.73 (*m*, H–C(5′)); 3.67–3.44 (*m*, 5 H); 3.06 (*q*, *J* = 7.2, H–C(14)); 2.23 (*dd*, *J* = 4.4, 13.4, H–C(7)); 2.01 (*ddd*, *J* = 4.1, 13.6, 14.3, H′–C(7)); 1.81 (*dd*, *J* = 4.3, 14.3, H–C(8)); 1.21 (*d*, *J* = 7.2, Me–C(14)); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, CD_3OD): *Table 2*; 178.5 (*s*); 173.1 (*s*); 172.8 (*s*); 111.2 (*d*); 100.3 (*s*); 73.4 (*s*); 69.8 (*s*); 50.2 (*d*); 43.4 (*d*); 38.3 (*t*); 33.4 (*s*); 29.9 (3*q*); 8.1 (*q*).

4. *Treatment of Ginkgolide B* (**1b**) *with 2 equiv. of* **2**. A soln. of **1b** (97.2 mg, 0.23 mmol) in THF (2 ml) was treated with a soln. of **2** (135 mg, 0.25 mmol) in THF (1 ml) at 30°, stirred for 1 h, treated with a soln. of **2** (119 mg, 0.22 mmol) in THF (0.9 ml), and stirred for 17 h at 30°. Evaporation, filtration through SiO_2 (AcOEt) and HPLC (hexane/AcOEt 2:1; 6 ml/min) gave **14** (20.7 mg, 6%), **21** (6.7 mg, 2%), **13** (32.6 mg, 10%), **22**/**23** (8.1 mg, 2%), **17** (8.9 mg, 3%; t_R 17.6), **7** (35.8 mg, 17%), **16** (15.6 mg, 5%; t_R 18.6), **8** (34.9 mg, 16%), **5** (26.3 mg, 12%), and **15** (5.6 mg, 2%; t_R 29.9).

3,10-Bis-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)ginkgolide B (**13**): HPLC: t_R (hexane/AcOEt 4:1, 9 ml/min) 29.8 min. IR ($CHCl_3$): 3492*w*, 3090*w*, 3067*w*, 3008*m*, 2873*m*, 1951*w*, 1793*s*, 1606*w*, 1497*m*, 1454*m*, 1406*w*, 1361*m*, 1326*m*, 1314*m*, 1279*w*, 1152*s*, 1072*s*, 1028*s*, 988*m*, 968*m*, 903*m*. ^{1}H-NMR (300 MHz, (D_6)acetone): *Table 1*; 7.46–7.24 (*m*, 40 arom. H); 6.17 (*s*, H–C(12)); 5.30 (br. *s*, H–C(6)); 5.22 (*d*, *J* = 7.2, H–C(2)); 5.05 (*d*, *J* = 11.5), 4.93 (*d*, *J* = 11.2), 4.81–4.64 (*m*), 4.60 (*d*, *J* = 12.1), 4.51 (*d*, *J* = 11.8, 16 PhC*H*); 3.89 (*t*, *J* = 8.4, H–C(3′)); 3.86–3.63 (*m*, irrad. at 5.27 → *d*, *J* = 9.0, H–C(2′), 8 H); 3.43–3.40 (*m*, H–C(5″)); 3.40 (*dd*, *J* = 7.8, 8.7, H–C(2″)); 3.12 (*q*, *J* = 6.8, H–C(14)); 2.02–1.80 (*m*, H–C(8), 2 H–C(7)); 1.44 (*d*, *J* = 6.5, Me–C(14)); 1.05 (*s*, *t*-Bu). FAB-MS: 1491 (100, $[M + Na]^+$), 1481 (28), 1469 (21, $[M + H]^+$), 1468 (37, M^+), 1467 (39), 1377 (12), 945 (11), 515 (19), 425 (15), 271 (23), 181 (47), 91 (32).

3-O-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)-10-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)ginkgolide B (**14**): HPLC: t_R (hexane/AcOEt 4:1, 9 ml/min) 34.0 min. IR ($CHCl_3$): 3395*w*, 3090*w*, 3067*m*, 3008*m*, 2923*m*, 2874*m*, 1951*w*, 1793*s*, 1606*w*, 1497*m*, 1454*m*, 1406*w*, 1362*m*, 1325*m*, 1275*w*, 1163*s*, 1070*s*, 1028*s*, 987*s*, 920*m*, 902*m*. ^{1}H-NMR (300 MHz, (D_6)acetone): *Table 1*; 7.46–7.20 (*m*, 40 arom. H); 6.30 (*s*, H–C(12)); 5.34 (br. *d*, *J* = 3.7, H–C(6)); 5.10 (*d*, *J* = 10.6), 4.93 (*d*, *J* = 10.6), 4.84 (*d*, *J* = 10.6), 4.81–4.50 (*m*, 16 PhC*H*); 3.89–3.71 (*m*, 8 H); 3.67 (*t*, *J* = 8.7, H–C(3″)); 3.55 (br. *d*, *J* = 10.0, H′–C(6′)); 3.43–3.40 (*m*, H–C(5″)); 3.38 (*dd*, *J* = 7.5, 8.7, H–C(2″)); 3.12 (*q*, *J* = 6.8, H–C(14)); 2.22 (*dd*, *J* = 3.9, 12.9, H–C(7)); 1.98 (*ddd*, *J* = 4.0, 13.1, 14.2, H′–C(7)); 1.85 (*dd*, *J* = 3.7, 14.3, H–C(8)); 1.44 (*d*, *J* = 6.8, Me–C(14)); 1.17 (*s*, *t*-Bu). FAB-MS: 1613 (15), 1491 (33, $[M + Na]^+$), 1469 (12, $[M + H]^+$), 1468 (22, M^+), 1467 (24), 756 (16), 515 (14), 425 (11), 415 (10), 307 (17), 303 (12), 302 (25), 301 (12), 271 (29), 181 (100), 91 (100).

3-O-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl)-10-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)ginkgolide B (**15**): IR ($CHCl_3$): 3532*w*, 3090*w*, 3066*w*, 3008*m*, 2926*m*, 2874*m*, 1951*w*, 1795*s*, 1706*w*, 1603*w*, 1497*m*, 1454*m*, 1404*w*, 1361*m*, 1324*w*, 1313*w*, 1261*m*, 1139*m*, 1072*s*, 1028*m*, 989*m*, 966*m*, 904*w*. ^{1}H-NMR (300 MHz, (D_6)acetone): *Table 1*; 7.43–7.22 (*m*, 40 arom. H); 6.19 (*s*, H–C(12)); 5.27 (*d*, *J* = 3.4, H–C(6)); 4.97 (*d*, *J* = 11.8), 4.93 (*d*, *J* = 11.8), 4.92 (*d*, *J* = 10.6), 4.87–4.73 (*m*), 4.68–4.48 (*m*, 16 PhC*H*); 3.99–3.94 (*m*, 1 H); 3.82–3.55 (*m*, 9 H); 3.39 (*dd*, *J* = 4.2, 7.3, irrad. at 4.80 → *m*, H–C(2′)); 3.38 (*dd*, *J* = 6.5, 7.3, 1 H); 3.37

(*dd*, J = 7.8, 8.7, irrad. at 4.50 → *d*, J = 9.0, H–C(2″)); 3.05 (*q*, J = 6.8, H–C(14)); 2.16–1.74 (*m*, 3 H); 1.41 (*d*, J = 6.8, Me–C(14)); 1.14 (*s*, *t*-Bu).

*1,3-Bis-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)ginkgolide B* (**16**): IR ($CHCl_3$): 3549*w*, 3465*w*, 3090*w*, 3066*w*, 3008*m*, 2873*m*, 1952*w*, 1796*s*, 1702*w*, 1604*w*, 1497*m*, 1454*m*, 1406*m*, 1361*m*, 1322*m*, 1278*w*, 1177*m*, 1148*s*, 1082*s*, 1028*s*, 987*m*, 956*m*, 923*m*, 905*m*. ^{1}H-NMR (300 MHz, (D_6)acetone): *Table 1*; 7.44–7.16 (*m*, 40 arom. H); 6.15 (*s*, H–C(12)); 5.43–5.42 (*m*, H–C(6)); 4.97 (*d*, J = 11.5), 4.90 (*d*, J = 10.9), 4.85 (*d*, J = 11.2), 4.83 (*d*, J = 11.2), 4.80–4.68 (*m*), 4.62 (*d*, J = 12.5), 4.61 (*d*, J = 12.1), 4.48 (*d*, J = 11.8, 16 PhC*H*); 3.93 (br. *d*, J = 2.2, 2 H–C(6′)); 3.83 (*dd*, J = 9.0, 9.7, H–C(4′)); 3.74–3.63 (*m*, irrad. at 3.83 → *m*, H–C(3′), 3 H); 3.55–3.46 (*m*, irrad. at 3.83 → *m*, H–C(5′), irrad. at 4.81 → *m*, H–C(2′), irrad. at 3.37 → *m*, H–C(3″)); 3.37 (*dd*, J = 7.5, 9.0, irrad. at 4.65 → *d*, J = 9.0, H–C(2″)); 3.25 (*m*, H–C(5″)); 3.22 (*q*, J = 6.8, H–C(14)); 1.89 (*dd*, J = 6.5, 12.4, H–C(7)); 1.41 (*d*, J = 7.1, Me–C(14)); 1.09 (*s*, *t*-Bu).

*1-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranosyl)-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)ginkgolide B* (**17**): IR ($CHCl_3$): 3392*m*, 3090*m*, 3066*m*, 3008*m*, 2917*m*, 2874*m*, 1952*w*, 1795*s*, 1605*w*, 1497*m*, 1454*m*, 1406*m*, 1360*m*, 1325*m*, 1313*m*, 1284*m*, 1154*s*, 1070*s*, 1028*s*, 986*s*, 961*m*, 923*m*. ^{1}H-NMR (300 MHz, (D_6)acetone): *Table 1*; 7.45–7.22 (*m*, 40 arom. H); 6.13 (*s*, H–C(12)); 5.58 (*m*, H–C(6)); 4.98 (*d*, J = 11.2), 4.96–4.75 (*m*, 9 PhC*H*); 4.65–4.58 (*m*, irrad. at 5.28 → *m*, H–C(1), 6 PhC*H*); 4.48 (*d*, J = 11.5, PhC*H*); 4.21 (br. *dt*, H–C(5′)); 3.98 (*t*, J = 9.6, H–C(3′)); 3.72–3.67 (*m*, 5 H); 3.62 (*dd*, J = 3.7, 9.6, H–C(2′)); 3.58 (*t*, J = 9.0, H–C(4′)); 3.47 (*t*, J = 9.0, irrad. at 3.35 → *d*, J = 9.3, H–C(3″)); 3.35 (*dd*, J = 7.5, 9.0, H–C(2″)); 3.15 (*q*, J = 7.0, H–C(14)); 3.04 (br. *dt*, H–C(5″)); 2.16–2.14 (*m*, H–C(7)); 1.93–1.84 (*m*, H′–C(7)); 1.39 (*d*, J = 6.9, Me–C(14));1.36–1.29 (*m*, H–C(8)); 1.13 (*s*, *t*-Bu).

5. *Debenzylations:* **18**–**20**. *3, 10-Di-*O*-(β-*D*-glucopyranosyl)ginkgolide B* (**18**). A mixture of **13** (37.9 mg, 0.026 mmol) and 10% Pd/C (50 mg) in MeOH (3.0 ml) and acetone (1.0 ml) was hydrogenated at 2.3 atm for 17 h. Filtration and evaporation gave **18** (18.3 mg, 95%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.19. ^{1}H-NMR (300 MHz, CD_3OD): *Table 1*; 6.15 (*s*, H–C(12)); 5.52 (*d*, J = 4.0, H–C(6)); 3.88 (*dd*, J = 1.6, 12.5, 1 H); 3.75 (*dd*, J = 2.3, 12.5, 1 H); 3.67 (*dd*, J = 5.8, 12.5, 1 H); 3.61 (*dd*, J = 4.7, 12.2, 1 H); 3.43–3.14 (*m*, 8 H); 3.02 (*q*, J = 6.8, H–C(14)); 2.27 (*dd*, J = 4.4, 13.4, H–C(7)); 2.03 (*ddd*, J = 4.4, 14.0, 14.6, H′–C(7)); 1.89 (*dd*, J = 4.0, 14.6, H–C(8)); 1.33 (*d*, J = 6.8, Me–C(14)); 1.13 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, CD_3OD): *Table 2*; 178.9 (*s*); 172.7 (*s*); 172.1 (*s*); 111.8 (*d*); 100.5 (*s*); 74.0 (*s*); 69.6 (*s*); 51.2 (*d*); 43.9 (*d*); 38.0 (*t*); 33.2 (*s*); 29.7 (3*q*); 8.3 (*q*).

*3-*O*-(β-*D*-Glucopyranosyl)-10-*O*-(α-*D*-glucopyranosyl)ginkgolide B* (**19**). A mixture of **14** (36.1 mg, 0.025 mmol) and 10% Pd/C (50 mg) in MeOH (3.0 ml) and acetone (1.5 ml) was hydrogenated at 1.2 atm for 21 h. Filtration and evaporation gave **19** (18.3 mg, 99%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.21. ^{1}H-NMR (300 MHz, CD_3OD): *Table 1*; 6.17 (*s*, H–C(12)); 5.50 (*d*, J = 4.1, H–C(6)); 3.78–3.15 (*m*, 12 H); 3.08 (*q*, J = 6.8, H–C(14)); 2.24 (*dd*, J = 4.4, 13.7, H–C(7)); 2.02 (*ddd*, J = 4.0, 13.7, 14.0, H′–C(7)); 1.80 (*dd*, J = 4.0, 14.3, H–C(8)); 1.31 (*d*, J = 6.8, Me–C(14)); 1.12 (*s*, *t*-Bu).

*1,3-Di-*O*-(β-*D*-glucopyranosyl)ginkgolide B* (**20**). A mixture of **16** (17.1 mg, 0.012 mmol) and 10% Pd/C (50 mg) in MeOH (3.0 ml) and acetone (1.5 ml) was hydrogenated at 1.2 atm for 21 h. Filtration and evaporation gave **20** (8.5 mg, 97%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.19. ^{1}H-NMR (300 MHz, CD_3OD): *Table 1*; 6.08 (*s*, H–C(12)); 5.58 (br. *d*, J = 2.5, H–C(6)); 3.86 (*dd*, J = 2.5, 12.1, 1 H); 3.78 (*dd*, J = 2.2, 12.1, 1 H); 3.72 (*dd*, J = 5.0, 12.1, 1 H); 3.59 (*dd*, J = 5.3, 12.1, 1 H); 3.41–3.18 (*m*, 8 H); 3.11 (*q*, J = 7.2, H–C(14)); 2.24–2.10 (*m*, 2 H–C(7)); 1.89 (*dd*, J = 5.3, 13.1, H–C(8)); 1.32 (*d*, J = 7.2, Me–C(14)); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, CD_3OD): *Table 2*; 178.5 (*s*); 175.1 (*s*); 172.0 (*s*); 111.4 (*d*); 101.4 (*s*); 73.4 (*s*); 70.4 (*s*); 50.6 (*d*); 43.6 (*d*); 38.0 (*t*); 33.4 (*s*); 29.6 (3*q*); 9.2 (*q*).

6. *Treatment of Ginkgolide B* (**1b**) *with 3.5 equiv. of* **2**. At 25°, **1b** (27.0 mg, 0.064 mmol) was treated with a soln. of **2** (60 mg, 0.11 mmol) in THF (1.3 ml), stirred for 24 h, treated with a soln. of **2** (60 mg, 0.11 mmol) in THF (1.3 ml), and stirred for 20 h at 25°. Evaporation, filtration through SiO_2 (AcOEt) and HPLC (hexane/AcOEt 4:1) gave **21** (51 mg, 42%), **23** (16 mg, 13%), **22** (18.4 mg, 15%), and **14** (21.9 mg, 24%).

*1,3,10-Tris-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)ginkgolide B* (**21**): HPLC: t_R (hexane/AcOEt 2:1, 6 ml/min) 13.8 min. IR ($CHCl_3$): 3090*w*, 3066*m*, 3008*m*, 2913*m*, 2872*m*, 1951*w*, 1792*s*, 1702*w*, 1654*w*, 1606*w*, 1586*w*, 1497*m*, 1454*s*, 1400*w*, 1360*m*, 1314*m*, 1280*m*, 1148*s*, 1074*s*, 1028*s*, 987*s*, 905*w*. ^{1}H-NMR (300 MHz, (D_6)acetone): *Table 1*; 7.50–7.09 (*m*, 60 arom. H); 6.11 (*s*, H–C(12)); 5.66 (br. *s*, H–C(6)); 5.10 (br. *d*, J = 11.5), 4.99 (*d*, J = 11.2), 4.97 (*d*, J = 11.2), 4.88 (*d*, J = 11.2), 4.86 (*d*, J = 11.2), 4.77 (*d*, J = 11.2), 4.78–4.53 (*m*), 4.47 (*d*, J = 11.8), 4.43 (*d*, J = 11.2, 24 PhC*H*); 4.10 (*t*, J = 8.1, irrad. at 5.01 → *d*, J = 8.4, H–C(2″)); 4.00–3.94 (*m*, irrad. at 3.42 → *m*, H–C(3‴), 1 H); 3.86–3.66 (*m*, irrad. at 4.10 → *m*, H–C(3″), 9 H); 3.58 (*dd*, J = 7.9, 9.2, irrad. at 5.34 → *d*, J = 9.0, H–C(2′)); 3.57 (*t*, J = 9.0, 1 H); 3.46–3.39 (*m*, irrad. at 4.83 → *m*, H–C(2‴), 2 H); 3.28 (*q*, J = 7.2, H–C(14)); 1.91–1.85 (*m*, 1 H); 1.45 (*d*, J = 7.5, Me–C(14)); 0.98 (*s*, *t*-Bu). FAB-MS: 1900 (5, $[M + H - 91]^+$), 1467 (11), 1163 (10), 1073 (80), 647 (10), 515 (32), 425 (24), 361 (19), 271 (57), 181 (100), 91 (76).

*1,3-Bis-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-10-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-ginkgolide B* (**22**): HPLC: t_R (hexane/AcOEt 4:1, 10.5 ml/min) 46.6 min. IR ($CHCl_3$): 3089*w*, 3066*m*, 3008*m*, 2926*m*, 2872*m*, 1951*w*, 1791*s*, 1709*w*, 1604*w*, 1497*m*, 1454*m*, 1363*m*, 1312*m*, 1279*w*, 1073*s*, 1028*s*, 984*s*, 910*w*. ^{1}H-NMR (500 MHz, (D_6)acetone; assignment based on H,H-*COSY*): *Table 1*; 7.45–7.01 (*m*, 60 arom. H); 6.05 (*s*, H–C(12)); 5.44 (br. *d*, *J* = 3.6, H–C(6)); 5.26 (*d*, *J* = 10.7), 5.02 (*d*, *J* = 10.7), 4.99 (*d*, *J* = 11.1), 4.96 (*d*, *J* = 12.0), 4.95 (*d*, *J* = 10.6), 4.90 (*d*, *J* = 10.7), 4.83 (*d*, *J* = 11.4), 4.80 (*d*, *J* = 11.6), 4,78 (*d*, *J* = 11.4), 4.77 (*d*, *J* = 10.7), 4.69–4.59 (*m*), 4.48 (*d*, *J* = 12.6), 4.47 (*d*, *J* = 12.0), 4.45 (*d*, *J* = 11.3, 21 PhC*H*); 4.44 (*m*, H–C(3″)); 4.41 (*d*, *J* = 12.1), 4.38 (*d*, *J* = 11.3), 4.31 (*d*, *J* = 12.6, 3 PhC*H*); 4.06 (*t*, *J* = 9.7, H–C(4′)); 4.00 (*t*, *J* = 9.2, H–C(3″)); 3.99 (m_c, H–C(6′)); 3.94 (*dd*, *J* = 4.5, 10.6, H–C(2′)); 3.73–3.63 (*m*, H–C(3‴), H–C(5‴), 2 H–C(6‴), H–C(5′), H–C(4‴)); 3.59–3.55 (*m*, H–C4″), H–C(6′)); 3.45 (*dd*, *J* = 7.9, 9.4, H–C(2″)); 3.40 (br. *t*, *J* = 7.7, H–C(2‴)); 3.23 (*dd*, *J* = 3.7, 10.9, H–C(6″)); 3.18 (*q*, *J* = 7.8, H–C(14)); 3.14 (*dd*, *J* = 1.6, 11.0, H′–C(6″)); 2.95 (*m*, H–C(5″)); 1.76 (*dd*, *J* = 4.1, 14.6, H–C(7)); 1.44 (*d*, *J* = 7.8, Me-C(14)); 1.33 (*m*, H-C(8)); 1.14 (*dt*, *J* = 4.0, 14.2, H′–C(7)); 1.04 (*s*, *t*-Bu).

*1-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranosyl)-3,10-bis-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-ginkgolide B* (**23**): HPLC: t_R (hexane/AcOEt 4:1, 10.5 ml/min) 45.4 min. IR ($CHCl_3$): 3090*w*, 3066*m*, 3008*m*, 2913*m*, 2872*m*, 1951*w*, 1794*s*, 1605*w*, 1497*m*, 1454*m*, 1399*w*, 1360*m*, 1328*m*, 1310*m*, 1279*w*, 1145*s*, 1074*s*, 1028*s*, 1007*m*, 985*m*, 902*w*. ^{1}H-NMR (500 MHz, (D_6)acetone; assignment based on H,H-*COSY*): *Table 1*; 7.42–7.05 (*m*, 60 arom. H); 6.03 (*s*, H–C(12)); 5.36 (*d*, *J* = 3.7, H–C(6)); 5.17 (*d*, *J* = 10.6), 5.03 (*d*, *J* = 10.9), 4.99 (*d*, *J* = 11.7), 4.93 (*d*, *J* = 11.3), 4.88 (*d*, *J* = 11.2), 4.85 (*d*, *J* = 11.0), 4.80 (*d*, *J* = 12.5), 4.78 (*d*, *J* = 11.2), 4.74 (*d*, *J* = 11.2), 4.70 (*d*, *J* = 11.0), 4.66 (*d*, *J* = 11.9), 4.62 (*d*, *J* = 10.5), 4.60 (*d*, *J* = 11.0), 4.51 (*d*, *J* = 10.5), 4.50 (*d*, *J* = 11.7), 4.49 (*d*, *J* = 10.6), 4.47 (*m*), 4.43 (*d*, *J* = 12.1), 4.39 (*d*, *J* = 11.2), 4.37 (*d*, *J* = 12.0, 24 PhC*H*); 4.19–4.13 (*m*, H–C(5′), H–C(4‴), H–C(3′)); 3.97 (*t*, *J* = 7.8, H–C(2″)); 3.87 (*m*, H–C(4′)); 3.84 (*t*, *J* = 7.8, H–C(3″)); 3.82–3.67 (*m*, 7 H); 3.66 (*dd*, *J* = 4.4, 9.6, H–C(2′)); 3.46 (*dd*, *J* = 2.9, 10.8, 1 H); 3.40–3.38 (*m*, 1 H); 3.36 (*dd*, *J* = 7.6, 8.9, H–C(2‴)); 3.10 (*q*, *J* = 7.5, H–C(14)); 3.07 (*m*, 1 H); 1.94 (*dt*, *J* = 4.0, 14.1, H–C(7)); 1.75 (*dd*, *J* = 4.0, 14.4, H′–C(7)); 1.36 (*dd*, *J* = 4.1, 13.4, H–(8)); 1.30 (*d*, *J* = 7.5, Me–C(14)); 0.94 (*s*, *t*-Bu).

7. *1,3,10-Tri-*O*-(β-*D*-glucopyranosyl)ginkgolide B* (**24**). A mixture of **21** (53.0 mg, 0.027 mmol) and 10% Pd/C (50 mg) in MeOH (3.0 ml) and acetone (1.5 ml) was hydrogenated at 1.2 atm for 21 h. Filtration and evaporation gave **24** (23.5 mg, 97%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.07. ^{1}H-NMR (300 MHz, CD_3OD): *Table 1*; 6.05 (*s*, H–C(12)); 5.75 (*d*, *J* = 3.4, H–C(6)); 3.90–3.16 (*m*, 18 H); 3.08 (*q*, *J* = 7.5, H–C(14)); 2.30 (*dt*, *J* = 4.1, 14.0, H–C(7)); 2.18–2.11 (*m*, H′–C(7)); 1.91 (*dd*, *J* = 4.4, 14.3, H–C(8)); 1.32 (*d*, *J* = 6.8, Me–C(14)); 1.14 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, CD_3OD): *Table 2*; 177.8 (*s*); 172.8 (*s*); 172.1 (*s*); 109.8 (*d*); 104.8 (*s*); 76.1 (*s*); 70.8 (*s*); 51.7 (*d*); 43.1 (*d*); 37.6 (*t*); 33.1 (*s*); 30.2 (3*q*); 11.9 (*q*).

8. *Glucosides of Ginkgolide A. 10-*O*-Acetyl-ginkgolide* A (**25**). A soln. of **1a** (85 mg, 0.21 mmol) in pyridine (0.75 ml) was treated with Ac_2O (82 µl, 0.87 mmol). Addition of EtOH after 20 h at 25°, evaporation, and crystallization (acetone/MeOH) gave **25** (88 mg, 94%). R_f (hexane/acetone 3:2) 0.19. IR ($CHCl_3$): 3483*w*, 2960*w*, 1780*s*, 1602*w*, 1372*w*, 1325*w*, 1152*w*, ,1125*w*, 1104*w*, 1084*w*, 1062*w*, 994*w*, 940*w*, 899*w*. ^{1}H-NMR (200 MHz, (D_6)acetone): 6.29 (*s*, H–C(10)); 6.19 (*s*, H–C(12)); 5.31 (*s*, HO–C(3)); 5.04–5.01 (*m*, H–C(6)); 4.92 (*dd*, *J* = 7.5, 9.1, H–C(2)); 3.15 (*q*, *J* = 7.1, H–C(14)); 3.03 (*dd*, *J* = 7.5, 14.9, H–C(1)); 2.25 (*s*, AcO); 2.24–1.86 (m, H–C(1), 2 H–C(7), H–C(8)); 1.29 (*d*, *J* = 7.1, Me–C(14)); 1.12 (s, *t*-Bu).

*10-*O*-Acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)ginkgolide A* (**26**). A suspension of **25** (59 mg, 0.13 mmol) in THF (6 ml) was treated with a soln. of **2** (95 mg, 0.17 mmol) in THF (1 ml) and stirred for 3 h at 30°. Evaporation and crystallization (hexane/CH_2Cl_2/AcOEt) gave **26** (108.5 mg, 85%). HPLC (hexane/AcOEt 4:1) of the mother liquor gave a further 9.8 mg (8%) of **26**. M.p. 222°. R_f (hexane/acetone 3:2) 0.34. HPLC: t_R (hexane/AcOEt 4:1, 9 ml/min) 27.6. IR ($CHCl_3$): 3066*w*, 3008*w*, 2967*w*, 2874*w*, 1801*s*, 1605*w*, 1497*w*, 1454*w*, 1406*w*, 1373*w*, 1323*w*, 1276*w*, 1116*m*, 1074*s*, 997*m*, 957*m*, 900*w*. ^{1}H-NMR (300 MHz, (D_6)acetone): 7.44–7.22 (*m*, 20 arom. H); 6.34 (*s*, H–C(10)); 6.21 (*s*, H–C(12)); 5.60 (*dd*, *J* = 8.4, 9.0, H–C(2)); 5.01 (br. *d*, *J* = 3.1, H–C(6)); 4.92 (*d*, *J* = 10.6), 4.82 (*s*), 4.77 (*d*, *J* = 10.9, 4 PhC*H*); 4.72 (*d*, *J* = 7.5, H–C(1′)); 4.66 (*d*, *J* = 11.2), 4.65 (*d*, *J* = 11.5), 4.61 (*d*, *J* = 10.6), 4.51 (*d*, *J* = 11.8, 4 PhC*H*); 3.81–3.75 (*m*, H–C(4′), 2 H–C(6′)); 3.60 (*t*, *J* = 9.0, H–C(3′)); 3.41 (*dd*, *J* = 7.5, 9.0, H–C(2′)); 3.34 (*dt*, *J* = 2.2, 9.6, H–C(5′)); 3.20 (*q*, *J* = 6.8, H–C(14)); 3.17 (*dd*, *J* = 7.5, 14.9, H–C(1)); 2.25 (*s*, AcO); 2.21–2.16 (*m*, 2 H); 2.01–1.89 (*m*, 2 H); 1.43 (*d*, *J* = 6.8, Me–C(14)); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, (D_6)acetone): 176.4 (*s*); 170.4 (*s*); 169.6 (*s*); 169.1 (*s*); 140.0 (*s*); 139.9 (*s*); 139.7 (2*s*); 129.1–128.1 (several *d*); 111.8 (*d*); 101.9 (*s*); 99.3 (*d*); 94.4 (*s*); 85.7 (*d*); 85.2 (*d*); 82.6 (*d*); 82.2 (*d*); 78.0 (*d*); 75.9 (*t*); 75.7 (*d*); 75.5 (*t*); 75.2 (*t*); 73.9 (*t*); 70.3 (*d*); 69.6 (*s*); 68.3 (*t*); 66.8 (*s*); 49.8 (*d*); 41.9 (*d*); 38.1 (*t*); 37.5 (*t*); 32.8 (*s*); 20.5 (*q*); 8.4 (*q*); (*q*, Me_3C hidden by acetone). FAB-MS: 1944 (26, $[2M]^+$), 1063 (19), 995 (26, $[M + Na]^+$), 972 (42, $[M]^+$), 971 (74, $[M - 1]^+$), 541 (87), 415 (19), 271 (19), 217 (12), 181 (100). Anal. calc. for $C_{56}H_{60}O_{15}$ (973.07): C 69.12, H 6.21; found: C 68.87, H 6.21.

3-O-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)ginkgolide A (**27**). At 25°, **26** (110 mg, 0.11 mmol) in MeOH (5 ml) and CH_2Cl_2 (2 ml) was treated with a sat. soln. of NH_3 in MeOH (1.2 ml) and stirred for 1.5 h. Evaporation, FC (hexane/acetone 3:2), and HPLC gave 48 mg (46%) of **27**. R_f (hexane/acetone 3:2) 0.26. HPLC: t_R (hexane/acetone 3:2, 6 ml/min) 13.4. IR ($CHCl_3$): 3290*w*, 3008*w*, 2967*w*, 2874*w*, 1794*s*, 1497*w*, 1454*w*, 1362*w*, 1324*w*, 1144*m*, 1073*s*, 1028*m*, 995*m*, 953*m*, 903*w*. ^{1}H-NMR (300 MHz, (D_6)acetone): 7.43–7.25 (*m*, 20 arom. H); 6.13 (*s*, H–C(12)); 5.95 (*d*, *J* = 4.4, HO–C(10)); 5.54 (*t*, *J* = 8.4, H–C(2)); 5.22 (*d*, *J* = 4.1, H–C(10)); 4.95–4.91 (*m*, H–C(6), PhC*H*); 4.82 (*s*), 4.77 (*d*, J = 11.2, 3 PhC*H*); 4.72 (*d*, *J* = 7.5, H–C(1′)); 4.65 (*d*, *J* = 13.1), 4.61 (*d*, *J* = 10.9), 4.52 (*d*, *J* = 11.8, 4 PhC*H*); 3.81–3.74 (*m*, H–C(4′), 2 H–C(6′)); 3.61 (*t*, *J* = 9.0, H–C(3′)); 3.43–3.33 (*m*, H–C(2′), H–C(5′)); 3.21 (*q*, *J* = 6.8, H–C(14)); 3.03 (*dd*, *J* = 7.5, 14.9, H–C(1)); 2.30–1.91 (*m*, 4 H); 1.43 (*d*, *J* = 6.8, Me–C(14)); 1.15 (*s*, *t*-Bu).

3-O-(β-D-Glucopyranosyl)ginkgolide A (**28**). A mixture of **27** (47 mg, 0.05 mmol) and 10% Pd/C (90 mg) in MeOH (10 ml) was hydrogenated at 3 atm for 72 h. Filtration, evaporation and FC (AcOEt/MeOH/H_2O 8.5:1.5:1) gave **28** (25 mg, 84%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.43. ^{1}H-NMR (300 MHz, CD_3OD): 6.07 (*s*, H–C(12)); 5.50 (*dd*, *J* = 8.1, 9.0, H–C(2)); 5.04 (*s*, H–C(10)); 4.90 (*d*, *J* = 3.4, H–C(6)); 4.50 (*d*, *J* = 7.5, H–C(1′)); 3.75 (*dd*, *J* = 2.2, 12.1, H–C(6′)); 3.60 (*dd*, *J* = 4.8, 12.1, H′–C(6′)); 3.35–3.15 (*m*, 5 H); 2.93 (*dd*, *J* = 7.5, 14.9, H–C(1)); 2.29–2.11 (*m*, 2 H); 2.00–1.85 (*m*, 2 H); 1.33 (*d*, *J* = 6.8, Me–C(14)); 1.10 (*s*, *t*-Bu). FAB-MS: 1163 (6, $[2M + Na]^+$), 593 (100, $[M + Na]^+$), 571 (23, $[M + H]^+$), 409 (90).

10-O-Acetyl-3-O-(β-D-glucopyranosyl)ginkgolide A (**29**). A mixture of **26** (5 mg, 5 μmol) and 10% Pd/C (20 mg) in MeOH (10 ml) was hydrogenated at 2.5 atm for 12 h. Filtration and evaporation gave **29** (3.1 mg, 98%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.37. ^{1}H-NMR (300 MHz, CD_3OD): 6.24 (*s*, H–C(10)); 6.17 (*s*, H–C(12)); 5.55 (*dd*, *J* = 8.1, 8.7, H–C(2)); 4.97 (*d*, *J* = 3.7, H–C(6)); 4.51 (*d*, *J* = 7.5, H–C(1′)); 3.75 (*dd*, *J* = 2.2, 12.1, H–C(6′)); 3.61 (*dd*, *J* = 5.0, 12.1, H′–C(6′)); 3.35–3.13 (*m*, 5 H); 3.03 (*dd*, *J* = 7.5, 14.6, H–C(1)); 2.26–1.87 (*m*, 4 H); 1.34 (*d*, *J* = 6.8, Me–C(14)); 1.05 (*s*, *t*-Bu).

9. *Lactoside* **36**. *(E/Z)-2,3,6-Tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-glucose Oxime* (**30**). A soln. of 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-glucopyranose [21] (678 mg, 0.7 mmol) in 96% EtOH (10 ml) was treated with a filtered soln. of $NH_2OH \cdot HCl$ (820 mg, 12 mmol) and Na (272 mg, 12 mmol) in EtOH (30 ml), and stirred 2 h at 80°. Extraction ($CHCl_3$), filtration through cotton plug, evaporation, and FC (hexane/acetone 6.5:3.5) gave **30** (649 mg, 94%). R_f (hexane/acetone 3:2) 0.39. IR ($CHCl_3$): 3580*w*, 3470*w* (br.), 3089*w*, 3066*w*, 3007*m*, 2910*w*, 2869*m*, 1951*w*, 1876*w*, 1811*w*, 1749*w*, 1605*w*, 1496*w*, 1454*m*, 1367*w*, 1362*m*, 1307*w*, 1252*w*, 1091*s* (br.), 1028*m*, 913*w*. ^{1}H-NMR (200 MHz, $CDCl_3$, (*E*)/(*Z*) 70:30): 8.20–8.17 (br. *s*, 0.3 H), 7.99 (br. *s*, 0.7 H, NOH); 7.57 (*d*, *J* = 7.1, 0.7 H, H–C(1)); 7.37–7.29 (*m*, 35 arom. H); 6.99 (*d*, *J* = 7.2, 0.3 H, H–C(1)); 5.00 (*d*, *J* = 11.6, 0.7 H, PhC*H*); 4.83–3.42 (*m*, 27 H). FAB-MS: 988 (10, $[M + H]^+$), 181 (52), 91 (100).

(Z)-2,3,6-Tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-gluconhydroximo-1,5-lactone (**31**). At 25°, **30** (649 mg, 0.6 mmol) in MeOH (15 ml) was treated with MnO_2 (170 mg) and stirred 27 h. Filtration through *Celite*, evaporation, and FC (hexane/acetone 7:3) gave **31** (564 mg, 87%). R_f (hexane/acetone 7:3) 0.15. IR ($CHCl_3$): 3585*w*, 3451*w*, 3330*w* (br.), 3089*w*, 3066*w*, 3007*m*, 2917*w*, 2869*m*, 1951*w*, 1875*w*, 1811*w*, 1670*w*, 1643*w*, 1605*w*, 1496*m*, 1454*m*, 1363*m*, 1281*w*, 1077*s* (br.),1028*m*, 928*m*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignment based on H,H-*COSY*): 7.34–7.18 (*m*, 35 arom. H); 6.86 (*d*, *J* = 1.3, exchange with CD_3OD, NOH); 4.93 (*d*, *J* = 11.5), 4.76 (*d*, *J* = 11.1), 4.71–4.65 (*m*, 6 PhC*H*); 4.59–4.56 (*m*, H–C(5), PhC*H*); 4.53–4.45 (*m*, 4 PhC*H*); 4.41 (*d*, *J* = 6.9, H–C(1′)); 4.39 (*d*, *J* = 12.0), 4.32 (*d*, *J* = 11.7), 4.29 (*d*, *J* = 11.7, 3 PhC*H*); 4.12 (*t*, *J* = 2.7, H–C(3)); 4.07 (*dd*, *J* = 2.9, J = 10.0, H–C(4)); 4.04 (*d*, *J* = 2.0, H–C(2)); 3.88 (br. *d*, *J* = 2.4, H–C(4′)); 3.75 (*dd*, *J* = 7.8, 9.8, H–C(2′)); 3.72 (*d*, *J* = 3.3, 2 H–C(6)); 3.57 (*dd*, *J* = 7.7, 8.7, H–C(6′)); 3.44 (*dd*, *J* = 5.4, 8.7, H′–C(6′)); 3.42–3.38 (*m*, H–C(3′), H–C(5′)). ^{13}C-NMR (125 MHz, $CDCl_3$): 151.27 (*s*); 138.74 (*s*); 138.62 (*s*); 138.41 (*s*); 138.10 (*s*); 137.88 (*s*); 137.79 (*s*); 137.22 (*s*); 128.45–127.50 (35*d*); 104.38 (*d*); 82.33 (*d*); 80.12 (*d*); 79.38 (*d*); 77.68 (*d*); 76.17 (*d*); 75.24 (*t*); 74.73 (*t*); 73.47 (*t*); 73.44 (*d*); 73.20 (*d*); 73.16 (*t*); 72.84 (*t*); 71.59 (*t*); 70.48 (*t*); 68.41 (*t*); 67.79 (*t*). FAB-MS: 986 (2, $[M + H]^+$), 554 (6), 181 (39), 91 (100). Anal. calc. for $C_{61}H_{63}NO_{11}$ (986.12): C 74.29, H 6.44, N 1.42; found: C 74.50, H 6.50, N 1.16.

[2,3,6-Tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-glucopyranosylidene]amino Methanesulfonate (**32**). At 0° and under Ar, **31** (557 mg, 0.5 mmol) in CH_2Cl_2 (10 ml) was treated with Et_3N (0.2 ml, 1.4 mmol) and MsCl (50 μl, 0.6 mmol). The reaction was quenched by the addition of a sat. $NaHCO_3$ soln. after 20 min. Extraction (CH_2Cl_2), filtration through cotton plug, evaporation, and FC (hexane/acetone 7:3) gave **32** (598 mg, 99%). R_f (hexane/acetone 7:3) 0.21. IR ($CHCl_3$): 3089*w*, 3066*w*, 3007*w*, 2916*w*, 2870*w*, 1952*w*, 1876*w*, 1811*w*, 1654*w*, 1605*w*, 1496*m*, 1454*s*, 1368*s*, 1362*w*, 1295*w*, 1177*s*, 1077*s* (br.), 1027*m*, 968*m*, 911*w*, 844*m*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignment based on H,H-*COSY*): 7.34–7.18 (*m*, 35 arom. H); 4.94 (*d*, *J* = 11.5), 4.77 (*d*, *J* = 11.1), 4.71–4.67 (*m*, 6 PhC*H*); 4.62 (*ddd*, *J* = 2.7, 3.2, 10.0, H–C(5)); 4.59 (*d*, *J* = 11.9), 4.52 (*d*, *J* = 12.3),

4.51 (*d*, *J* = 11.8), 4.47 (*d*, *J* = 11.7), 4.42 (*d*, *J* = 12.3, 5 PhC*H*); 4.41 (*d*, *J* = 7.7, H–C(1')); 4.32 (*d*, *J* = 11.8), 4.29 (*d*, *J* = 11.7, 2 PhC*H*); 4.18 (*t*, *J* = 2.6, H–C(3)); 4.11 (*dd*, *J* = 0.4, 2.4, H–C(2)); 4.10 (*dd*, *J* = 2.5, 9.5, H–C(4)); 3.89 (br. *d*, *J* = 2.9, H–C(4')); 3.76 (*dd*, *J* = 7.7, 9.7, H–C(2')); 3.74–3.68 (*m*, 2 H–(C(6)); 3.56 (*dd*, *J* = 6.6, 7.9, H–C(6')); 3.46 (*dd*, *J* = 5.4, 7.9, H'–C(6')); 3.44 (*m*, H–C(5')); 3.43 (*dd*, *J* = 2.9, 9.7, H–C(3')); 3.04 (*s*, Me). ^{13}C-NMR (125 MHz, $CDCl_3$): 157.53 (*s*); 138.64 (*s*); 138.47 (*s*); 138.32 (*s*); 137.89 (*s*); 137.69 (*s*); 137.53 (*s*); 136.48 (*s*); 128.51–127.54 (35 *d*); 104.68 (*d*); 82.27 (*d*); 79.37 (*d*); 79.30 (*d*); 77.60 (*d*); 77.23 (*d*); 75.31 (*t*); 74.76 (*t*); 73.47 (*t*); 73.32 (*d*); 73.11 (*t*); 72.90 (*t*); 71.74 (*t*); 71.19 (*t*); 68.47 (*t*); 67.01 (*t*); 36.04 (*q*). FAB-MS: 970 (1), 632 (2), 542 (1), 271 (4), 181 (41), 91 (100).

*2,5-Anhydro-2,3,6-tri-*O*-benzyl-1-hydrazi-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-galactopyranosyl)-*D*-glucitol* (**33**). At 25°, **32** (247 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) was treated with a sat. NH_3 soln. in MeOH (50 ml) and stirred for 24 h in a closed vessel. Evaporation and crystallization (Et_2O) gave **33** (171 mg, 78%). FC (hexane/AcOEt 6.5:3.5) of the mother liquor gave a further 26 mg (12%) of **33**. R_f (hexane/AcOEt 6.5:3.5) 0.33. M.p. 81–83°. IR ($CHCl_3$): 3270*w*, 3089*w*, 3066*w*, 3007*m*, 2871*m*, 1951*w*, 1876*w*, 1810*w*, 1750*w*, 1648*w*, 1605*w*, 1496*m*, 1454*m*, 1397*w*, 1362*m*, 1273*m*, 1077*s*, 1028*m*, 909*m*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignment based on H,H-*COSY*): 7.37–7.11 (*m*, 35 arom. H); 5.05 (*d*, *J* = 10.6), 4.97 (*d*, *J* = 11.4), 4.79 (*d*, *J* = 11.2), 4.78 (*d*, *J* = 10.7), 4.73–4.65 (*m*), 4.55 (*d*, *J* = 11.5), 4.54 (*d*, *J* = 12.0, 11 PhC*H*); 4.38 (*d*, *J* = 7.7, H–C(1')); 4.37 (*d*, *J* = 11.8), 4.33 (*d*, *J* = 12.0), 4.26 (*d*, *J* = 11.8, 3 PhC*H*); 4.19 (*dd*, *J* = 9.1, 10.0, H–C(4)); 4.02 (*d*, *J* = 9.4, H–C(2)); 3.89 (*d*, *J* = 2.6, H–C(6)); 3.88 (*d*, *J* = 2.7, H–C(4')); 3.74 (*dd*, *J* = 7.7, 9.7, H–C(2')); 3.67 (*dt*, *J* = 1.9, 2.5, 9.9, H–C(5)); 3.56 (*dd*, *J* = 9.1, 9.2, H–C(3)); 3.55 (*t*, *J* = 8.9, H'–C(6)); 3.53 (*d*, *J* = 1.8, H–C(6')); 3.39 (*dd*, *J* = 5.1, 9.0, H'–C(6')); 3.34 (*dd*, *J* = 2.9, 9.7, H–C(3')); 3.33 (*ddd*, *J* = 0.7, 5.9, 8.1, H–C(5')); 2.67 (*d*, *J* = 9.4, NH); 2.31 (*d*, *J* = 9.4, NH). ^{13}C-NMR (125 MHz, $CDCl_3$): 139.06 (*s*); 138.89 (*s*); 138.65 (*s*); 138.52 (*s*); 138.15 (*s*); 137.91 (*s*); 137.86 (*s*); 128.38–127.20 (35 *d*); 102.69 (*d*); 83.05 (*s*); 82.59 (*d*); 82.44 (*d*); 79.86 (*d*); 76.83 (*d*); 75.90 (*d*); 75.71 (*t*); 75.57 (*t*); 75.31 (*t*); 74.73 (*t*); 73.68 (*d*); 73.42 (*t*); 73.14 (*t*); 73.08 (*d*); 72.59 (*t*); 68.12 (*t*); 67.33 (*t*). FAB-MS: 985 (7, $[M + H]^+$), 271 (3), 181 (39), 91 (100). Anal. calc. for $C_{61}H_{64}N_2O_{10}$ (985.13): C 74.37, H 6.55, N 2.84; found: C 74.32, H 6.46, N 2.69.

*2,5-Anhydro-1-azi-2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-galactopyranosyl)-*D*-glucitol* (**34**). At −45°, **33** (230 mg, 0.2 mmol) in CH_2Cl_2 (20 ml) and Me_3N (0.5 ml) were treated dropwise under Ar with a soln. of I_2 (59 mg, 0.2 mmol) in CH_2Cl_2 (5 ml) for 1.5 h. After the addition, the mixture was filtered through SiO_2 (CH_2Cl_2), evaporated at 0° and dried at 45° *i.v.*: **34** (224 mg, 97%). R_f (hexane/AcOEt 2:1) 0.52. IR ($CHCl_3$): 3089*w*, 3066*m*, 3007*m*, 2871*m*, 1951*w*, 1876*w*, 1811*w*, 1752*w*, 1645*w*, 1606*w*, 1563*w*, 1497*m*, 1454*s*, 1399*w*, 1363*m*, 1307*m*, 1264*m*, 1077*s*, 1028*m*, 912*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.11 (*m*, 35 arom. H); 5.07 (*d*, *J* = 10.7), 5.00 (*d*, *J* = 11.5), 4.85 (*d*, *J* = 11.2), 4.76 (*d*, *J* = 11.2), 4.74–4.73 (*m*), 4.70 (*d*, *J* = 10.5), 4.58 (*d*, *J* = 11.3), 4.49 (*d*, *J* = 12.1, 9 PhC*H*); 4.41 (*d*, *J* = 7.7, H–C(1')); 4.39 (*d*, *J* = 11.8), 4.31 (*d*, *J* = 11.3), 4.30 (*d*, *J* = 12.1), 4.28 (*d*, *J* = 11.8), 4.22–4.16 (*d*, *J* = 10.9, 5 PhC*H*); 4.05 (*d*, *J* = 9.1, H–C(2)); 3.94 (br. *d*, *J* = 2.8, 1 H); 3.87 (*t*, *J* = 8.9, H–C(3)); 3.84–3.77 (*m*, 3 H); 3.65–3.53 (*m*, 2 H); 3.43–3.35 (*m*, 4 H).

*10-*O*-Acetyl-3-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]ginkgolide A* (**35**). A suspension of **25** (26 mg, 58 μmol) in THF (5 ml) was treated with a soln. of **34** (62 mg, 64 μmol) in THF (0.8 ml) and stirred for 3 h at 25°. Evaporation and HPLC (hexane/acetone 3:2) gave **35** (75 mg, 92%). R_f (hexane/acetone 3:2) 0.42. HPLC: t_R (hexane/acetone 3:2, 6 ml/min) 12.8. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.03 (*m*, 35 arom. H); 6.10 (*s*), 6.05 (*s*, H–C(10), H–C(12)); 5.16–5.08 (*m*, 2 H); 4.95 (*d*, *J* = 11.2, PhC*H*); 4.83–4.33 (*m*, 15 H); 4.25 (*d*, *J* = 12.0, PhC*H*); 4.10 (*t*, *J* = 9.1, 1 H); 3.90–3.34 (*m*, 10 H); 3.17–3.06 (*m*, 2 H); 2.70 (*dd*, *J* = 7.5, 14.9, H–C(1)); 2.21 (*s*, AcO); 2.15–1.73 (*m*, 4 H); 1.45 (*d*, *J* = 6.6, Me–C(14)); 1.04 (*s*, *t*-Bu).

*10-*O*-Acetyl-3-*O*-[4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]ginkgolide A* (**36**). A mixture of **35** (20 mg, 14 μmol) and 10% Pd/C (100 mg) in MeOH (5 ml) was hydrogenated at 3 atm for 17 h. Filtration and evaporation gave **36** (11 mg, 99%). R_f (AcOEt/MeOH/H_2O 8.5:1.5:1) 0.15. ^{1}H-NMR (300 MHz, CD_3OD): 6.24 (*s*), 6.17 (*s*, H–C(10), H–C(12)); 5.53 (*t*, *J* = 8.4, H–C(2)); 4.98 (*d*, *J* = 3.7, H–C(6)); 4.53 (*d*, *J* = 7.5, H–C(1')); 4.36 (*d*, *J* = 7.2, H–C(1'')); 3.81–3.24 (*m*, 12 H); 3.15 (*q*, *J* = 6.8, H–C(14)); 3.03 (*dd*, *J* = 7.8, 14.6, H–C(1)); 2.26–2.21 (*m*, 1 H); 2.21 (*s*, AcO); 2.09 (*dt*, *J* = 4.0, 13.7, H–C(7)); 1.98–1.86 (*m*, 2 H); 1.35 (*d*, *J* = 6.8, Me–C(14)); 1.05 (*s*, *t*-Bu).

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