GLYCOSYLATION OF TRITERPENE ALCOHOLS AND ACIDS OF THE LUPANE AND A-SECOLUPANE SERIES*

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A series of 3- and 28-glucosides and glucosyl esters of betulinic acid (**1a**), 28-hydroxy-3,4-secolupa-4(23),20(29)-dien-3-oic acid (**22a**), dimethyl ester of 28-hydroxy-2,3-secolup-20(29)-en-2,3-dioic acid (**43a**), their 20(29)-dihydro derivatives (**1b**, **22b**, **43b**) and several other triterpenes of the lupane (**12a**, **12b**) and 3,4-secolupane series (**18a**, **18b**, **32a**) has been prepared by reaction of tetra-*O*-acetyl-α-D-glucopyranosyl bromide in acetonitrile in the presence of mercury(II) cyanide and subsequent deacetylation of the obtained tetra-*O*-acetyl-β-D-glucopyranosyl derivatives. In several cases attempted glucosylation in the presence of silver silicate afforded predominantly the corresponding 1,2-orthoacetates of α-D-glucopyranose.

Key words: Lupane; 3,4-Secolupane; 2,3-Secolupane; Betulinic acid; Glucoside; ^{1}H and ^{13}C NMR spectra.

The recently found biological activity of betulinic acid (**1a**), its derivatives, and other triterpenoids with lupane and A-secolupane skeleton (see *e.g.* refs[2–9] and references therein) aroused an increased interest in the preparation of their derivatives (*inter alia* glycosides) that might exhibit biological activity. Glycosides of some lupane derivatives have been prepared already earlier (see refs[10,11] and references therein).

In the present paper we describe the preparation of glucosides of less common triterpenic compounds (A-secoacids and other A-secolupane derivatives) and of betulinic acid. Glucosides were prepared from aglycons of two parallel series: compounds with an isopropenyl side chain in position 19 (series **a**; 20(29)-lupene derivatives) and the analogous dihydro derivatives with an isopropyl group in the position 19 (series **b**; lupane derivatives).

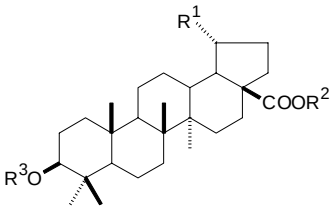
* Part CVII in the series Triterpenes; Part CVI: see ref.[1].

Except the common compounds[12] (betulinic acid (**1a**), dihydrobetulinic acid (**1b**) and their derivatives **2a**, **2b**, **3a** and **3b**), the starting aglycones were prepared from the known[13] 28-acetoxy-20(29)-lupen-3-one (**13a**) and 28-acetoxylupan-3-one (**13b**). The preparation of 2,3-secodiacids **42a** and **42b** and their methyl esters **43a** and **43b** has already been published[13], the 3,4-secolupane derivatives were synthesized by procedures described in analogous cases[14,15]: ketones **13a** and **13b** were converted into oximes **14a** and **14b** which on Beckmann rearrangement afforded acetoxy nitriles **19a** and **19b** (compounds **14a**, **14b**, **19a** and **19b** are described in the literature[16]). Mild alkaline hydrolysis of acetoxy nitriles gave 28-hydroxy nitriles **18a** and **18b**, hydrolysis with 10% sodium hydroxide in boiling ethylene glycol furnished 3,4-secoacids **22a** and **22b**. These were further converted into methyl esters **23a** and **23b**, acetates **24a** and **24b** and methyl ester acetates **25a** and **25b**. Reduction of methyl ester acetate **25a** with lithium aluminium hydride afforded diol **32a**, characterized as diacetate **33a** (the compounds **23b**, **32a** and **33a** have been obtained earlier[17–19] by other procedures). An attempted partial acetylation of diol **32a** with acetic anhydride in pyridine at –30 °C gave a mixture of diacetate **33a**, diol **32a** and monoacetates **34a** and **35a**. The isomeric monoacetates **34a** and **35a** were obtained only as a 1 : 1 mixture (^{1}H NMR spectrum) and resisted attempted separation by chromatography or crystallization.

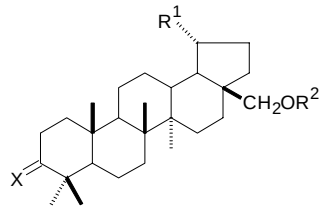
Of the known glycosidation procedures[20] for the preparation of glucoside tetraacetates, we tried the Koenigs–Knorr reaction with tetra-*O*-acetyl-α-D-glucopyranosyl bromide in the presence of silver silicate for the reaction of ketone **12a**, methyl ester of 3,4-secoacid **23a** and dimethyl esters of 2,3-secodiacids **43a** and **43b**. However, we obtained the corresponding orthoacetates (**15a**, **26a**, **45a** and **45b**), the yields of the desired glucoside tetraacetates being very low. The orthoacetates are unstable and decompose during purification or spectral measurements in chloroform under formation of mixtures containing (according to thin-layer chromatography) the starting aglycones and two tetra-*O*-acetyl derivatives of glucose. In the case of orthoacetate **26a** the decomposition products were identified by ^{1}H and ^{13}C NMR spectra as the aglycone **23a**, 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (the NMR data of both glucose tetraacetates agree well with the published ones[21,22]).

Much more successful for the preparation of glucoside tetraacetates proved to be the presence of a soluble catalyst - mercury(II) cyanide in acetonitrile. This method was already used for the synthesis of triterpenoid glycosides, *e.g.* lupane[10] and dammarane[23] derivatives. Using mercury(II) cyanide we obtained the 28-*O*-glucoside tetraacetates **16b**, **20a**, **20b**, **27a**, **27b**, **46a** and **46b**, and 3β-*O*-glucoside acetates **4a** and **4b**. In addition to the glucoside acetates, we often isolated from the reaction mixtures also the unreacted starting aglycones and in some cases their acetates; the formation of orthoacetates was not observed. From 3,4-seco-3,28-diol **32a** we obtained predominantly the bis-glucoside tetraacetate **36a** along with 3-*O*-glucoside tetraacetate **38a**; minor amounts of the isomeric glucoside tetraacetates **40a** and **41a** with acetylated hydroxyl

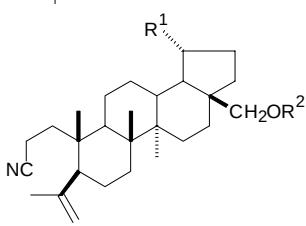
in the aglycone part (in position 3 and 28, respectively) were also found. These acetates were obtained as an unseparable 1 : 1 mixture (according to NMR spectra) and were identified by ^{1}H and ^{13}C NMR spectra of the mixture.



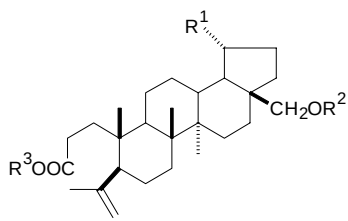
	R^2	R^3
1a, **1b**	H	H
2a, **2b**	CH_3	H
3a, **3b**	H	Ac
4a, **4b**	CH_3	$Glc(Ac)_4$
5a, **5b**	CH_3	Glc
6a, **6b**	Glc-orthoAc	Ac
7a, **7b**	$Glc(Ac)_4$	Ac
8a, **8b**	Glc	Ac
9a, **9b**	Glc	H
10a	$Glc(Ac)_4$	$Glc(Ac)_4$
11a	Glc	Glc



	R^2	X
12a, **12b**	H	O
13a, **13b**	Ac	O
14a, **14b**	Ac	NOH
15a	Glc-orthoAc	O
16a, **16b**	$Glc(Ac)_4$	O
17a, **17b**	Glc	O

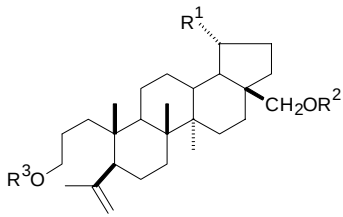


	R^2
18a, **18b**	H
19a, **19b**	Ac
20a, **20b**	$Glc(Ac)_4$
21a, **22b**	Glc

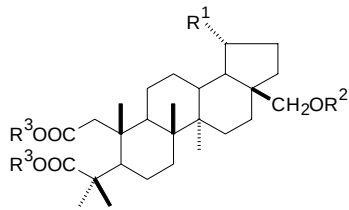


	R^2	R^3
22a, **22b**	H	H
23a, **23b**	H	CH_3
24a, **24b**	Ac	H
25a, **25b**	Ac	CH_3
26a	Glc-orthoAc	CH_3
27a, **27b**	$Glc(Ac)_4$	CH_3
28a, **28b**	Glc	CH_3
29a, **29b**	Glc	H
30a	Ac	$Glc(Ac)_4$

The same glycosylation protocol was also applied to the preparation of derivatives **7a** and **7b** in which the glucose moiety is bonded by ester bond to the carboxyl group. Glycosylation of acetylbetulinic acid (**3a**) and acetyldihydrobetulinic acid (**3b**) afforded, beside glucosyl acetates **7a** and **7b**, also orthoacetates **6a** and **6b**. They were identified by ^{1}H NMR spectra as an impurity in the crude reaction product. The mentioned glycosylation method proved to be unsuitable for the preparation of diglucosyl derivatives of betulinic acid (**1a**) and dihydrobetulinic acid (**1b**) because these acids are

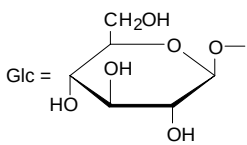


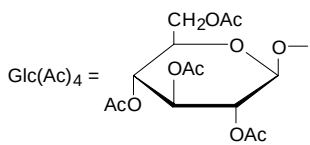
	R^2	R^3
32a	H	H
33a	Ac	Ac
34a	H	Ac
35a	Ac	H
36a	$Glc(Ac)_4$	$Glc(Ac)_4$
37a	Glc	Glc
38a	H	$Glc(Ac)_4$
39a	H	Glc
40a	Ac	$Glc(Ac)_4$
41a	$Glc(Ac)_4$	Ac

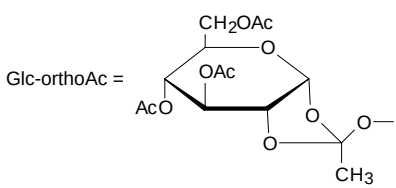


	R^2	R^3
42a, **42b**	H	H
43a, **43b**	H	CH_3
44a, **44b**	Ac	CH_3
45a, **45b**	Glc-othoAc	CH_3
46a, **46b**	$Glc(Ac)_4$	CH_3
47a, **47b**	Glc	CH_3

In formulae **1**-**47** : **a**, $R^1 = C(CH_3)=CH_2$
b, $R^1 = CH(CH_3)_2$







Ac = $COCH_3$

very sparingly soluble in acetonitrile or its mixtures with ether and chloroform. Dihydrobetulinic acid (**1b**) was recovered entirely unchanged from the reaction mixture, betulinic acid (**1a**) afforded small amounts of bis-glucosyl derivative **10a**.

Glucosides **5a**, **5b**, **8a**, **8b**, **11a**, **17a**, **17b**, **21a**, **21b**, **28a**, **28b**, **37a**, **39a**, **47a** and **47b** were obtained from the corresponding glucoside acetates by treatment with sodium methoxide in methanol at room temperature. Under these conditions only the acetate groups in the sugar part of the molecule were cleaved off whereas the ester groups in the aglycone part remained intact. The acetate group in position 3 of glucosides **8a** and **8b** was hydrolyzed with sodium hydroxide in methanol at 50 °C under formation of glucosides **9a** and **9b**. Analogous hydrolysis of the methyl ester group in the 3,4-seco derivatives **28a** and **28b** proceeded already at room temperature and afforded glucosides **29a** and **29b**; under same conditions the methyl ester groups in the 2,3-seco derivatives **47a** and **47b** were not hydrolyzed. Glucosides **9a** and **11a**, derived from betulinic acid (**1a**), have already been prepared by other methods[24–26].

Structure of the prepared compounds has been confirmed by infrared, NMR and mass spectra (electron impact spectra (EI-MS) in the case of aglycones and glucoside acetates, fast atom bombardment spectra (FAB-MS) in the case of glucosides). Electron impact spectra exhibited characteristic very abundant ions of *m/z* 331, 169 and 109, arising from the glucose units, in the higher mass region the fragmentation of these compounds corresponds to the known[13,15,27] fragmentation of the corresponding aglycone. In addition to ions $[M + Na]^+$ and $[M + H]^+$, FAB mass spectra of glucosides displayed fragment ions $[M + H - 162]^+$ and $[M + H - 180]^+$ corresponding to loss of glucosyl or glucosyloxyl group. Moreover, compounds with glucose esterically bonded to the carboxyl group in position 17 typically undergo cleavage of the C(17)-C(28) bond leading to ions $[M + H - 208]^+$. No meaningful FAB spectra were obtained in the case of diglucoside **37a**; however, its structure was confirmed by the ^{1}H NMR spectrum.

Proton NMR data for all the glucoside acetates prepared are summarized in Tables I–III, spectra of some glucosides (**5a**, **8a**, **11a**, **29a**, **37a**, **39a**) are given in Table IV. The values of the coupling constants $J(1',2')$ (about 8 Hz) show that all these derivatives have β-configuration at the anomeric carbon atom. In the case of orthoacetates **26a** and **45a**, the chemical shifts and coupling constants of protons in the glucose moiety (Tables II and III) agree with the data for analogous orthoacetates of the α-D-*gluco*-configuration[28,29]; the chemical shift of the singlet of the methyl group on the dioxolane ring (δ about 1.73) corresponds to the *endo*-configuration of this methyl group[29].

The assignment of chemical shifts in the ^{13}C NMR spectra of aglycones and glucoside acetates (Tables V and VI) is based on the APT spectra and comparison with the literature data[19,30,31] for aglycones **2a**, **12a**, **32a** and **33a** and for similar lupane derivatives and their glucoside acetates[10,11]. Attachement of tetra-*O*-acetyl-β-D-glucopyranosyl group to the 28-hydroxyl group results in a large downfield shift of the C-28 signal

TABLE I
Proton NMR data of compounds **4a**, **4b**, **7a**, **7b**, **10a**, **16a** and **16b** in $CDCl_3$

Proton	Chemical shifts (*coupling constants*)						
	4a	**4b**	**7a**	**7b**	**10a**	**16a**	**16b**[a]
				Aglycone moiety			
CH_3	0.714 s	0.719 s	0.826 s	0.831 s	0.711 s	0.936 s	0.948 bs
	0.809 s	0.819 s	0.833 s	0.839 s	0.809 s	0.982 s	0.960 bs
	0.887 s	0.893 s	0.841 s	0.850 s	0.876 s	1.036 s	1.041 s
	0.900 s	0.893 s	0.886 s	0.883 s	0.881 s	1.070 s	1.076 s
	0.947 s	0.927 s	0.948 s	0.929 s	0.939 s	1.078 s	1.083 s
H-2α	[b]	[b]	[b]	[b]	[b]	2.40 ddd	2.41 ddd
						15.8;7.6;4.4	*15.7;7.5;4.4*
H-2β	[b]	[b]	[b]	[b]	[b]	2.50 ddd	2.50 ddd
						15.8;9.7;7.6	*15.7;9.8;7.5*
H-3	3.05 dd	3.07 dd	4.46 dd	4.47 dd	3.06 dd	–	–
	11.5;4.5	*11.4; 4.8*	*~11.0;5.8*	*11.4;5.5*	*11.8;4.8*		
H-19	2.99 td	[b]	2.94 td	[b]	2.94 td	2.37 td	[b]
	10.8;10.8;4.6		*~11.1;11.1;4.6*		*~11.0;11.0;4.7*	*~10.8;10.8;5.8*	
H-28a	–	–	–	–	–	3.54 dd	3.52 dd
						9.2;1.3	*9.4;1.3*
H-28b	–	–	–	–	–	3.64 bd	3.61 bd
						9.2	*9.4*
H-29a	4.60 m		4.61 m		4.61 m	4.58 m	
		0.745 d		0.744 d			0.752 d
H-29b	4.72 bd	*7.0*	4.74 bd	*6.7*	4.74 bd	4.67 bd	*~6.7*
	~2.4		*~2.2*		*~2.4*	*~2.4*	
H-30	1.685 bs	0.850 d	1.678 bs	0.847 d	1.678 bs	1.670 bs	0.838 d
		7.0		*6.7*			*~6.7*
OMe	3.67 s	3.65 s	–	–	–	–	–
OAc	–	–	2.041 s	2.045 s	–	–	–
				Glucose moiety			
					10a[c]	**10a**[d]	
H-1	4.53 d	4.53 d	5.70 d	5.68 d	4.53 d	5.70 d	4.47 d	4.46 d
	7.8	*7.8*	*8.3*	*8.3*	*8.0*	*8.3*	*7.8*	*8.0*
H-2	5.03 dd	5.03 dd	5.21 dd	5.20 dd	5.02 dd	5.21 dd	5.02 dd	5.01 dd
	9.6;7.8	*9.6;7.8*	*9.5;8.3*	*9.6;8.3*	*9.7;8.0*	*9.7;8.3*	*9.6;7.8*	*9.7;8.0*
H-3	5.20 t	5.20 t	5.28 t	5.27 dd	5.20 t	5.28 t	5.23 t	5.22 dd
	~9.5;9.5	*~9.5;9.5*	*9.5;9.3*	*9.6;9.2*	*~9.5;9.5*	*~9.4;9.4*	*~9.6;9.6*	*9.7;9.4*
H-4	5.04 dd	5.05 dd	5.16 dd	5.16 dd	5.04 dd	5.16 dd	5.11 t	5.10 dd
	~10.0;9.5	*~10.0;9.5*	*~10.0;9.3*	*10.1;9.2*	*~10.0;9.5*	*9.8;9.3*	*~9.7;9.7*	*9.9;9.4*
H-5	3.68 ddd	3.68 ddd	3.83 ddd	3.82 ddd	3.68 ddd	3.83 ddd	3.70 ddd	3.70 ddd
	10.0;5.5;2.5	*10.0;5.5;2.5*	*10.0;4.4;2.4*	*10.1;4.4;2.4*	10.0;5.4;2.5	*10.2;4.4;2.4*	*10.0;4.6;2.4*	*9.9;4.6;2.6*
H-6b	4.11 dd	4.11 dd	4.07 dd	4.06 dd	4.11 dd	4.07 dd	4.15 dd	4.14 dd
	12.2;2.5	*12.2;2.5*	*12.4;2.4*	*12.4;2.4*	*12.3;2.5*	*12.5;2.4*	*12.0;2.4*	*12.2;2.6*
H-6b	4.25 dd	4.25 dd	4.32 dd	4.31 dd	4.24 dd	4.32 dd	4.30 dd	4.29 dd
	12.2;5.5	*12.2;5.5*	*12.4;4.4*	*12.4;4.4*	*12.3;5.5*	*12.5;4.4*	*12.0;4.6*	*12.2;4.6*
OAc	2.005 s	2.007 s	2.020 s	2.014 s	2.005 s	2.017 s	2.016 s	2.012 s
	2.023 s	2.025 s	2.024 s	2.019 s	2.022 s	2.023 s	2.024 s	2.019 s
	2.029 s	2.031 s	2.037 s	2.034 s	2.027 s	2.036 s	2.031 s	2.028 s
	2.072 s	2.077 s	2.078 s	2.075 s	2.073 s	2.075 s	2.102 s	2.097 s

[a] H-1β: 1.91 ddd (*J* = *13.3*; *7.5* and *4.4* Hz); [b] signal was not assigned; [c] 3-*O*-Glc(Ac)$_4$; [d] 28-*O*-Glc(Ac)$_4$.

TABLE II

Proton NMR data of compounds **18a**, **18b**, **20a**, **20b**, **23a**, **26a**, **27a**, **27b** and **30a** in $CDCl_3$

Proton	Chemical shifts (*coupling constants*)								
	18a	**18b**	**20a**	**20b**	**23a**	**26a**[a]	**27a**	**27b**	**30a**
					Aglycone moiety				
CH_3	0.838 s	0.850 s	0.846 s	0.857 s	0.827 s	0.830 s	0.834 s	0.845 s	0.818 s
	0.993 bs	0.976 bs	0.981 s	0.966 s	0.992 s	0.978 s	0.981 s	0.963 s	0.981 s
	1.071 s	1.078 s	1.078 s	1.086 s	1.066 s	1.075 s	1.073 s	1.080 s	1.068 s
H-2a	2.17 m	2.19 m	2.16 m	2.19 m	2.15 m	2.15 m	2.15 m	2.17 m	2.17 m
H-2b	2.31 m	2.32 m	2.31 m	2.32 m	2.33 m	2.33 m	2.33 m	2.34 m	2.37 m
H-19	2.39 td	[b]	2.37 td	[b]	2.39 td	2.37 td	2.36 td	[b]	2.45 td
	~11;11;5.8		*~11;11;5.7*		*~11;11;5.8*	*~10.8;10.8;5.5*	*~11;11;5.7*		*~11;11;5.7*
H-23a	4.64 bd	4.64 bd	4.65 bd	4.65 bd	4.65 bd	4.65 bd	4.66 bd	4.66 bd	4.64 bd
	~2.2	*~2.0*	*~2.0*	*~2.0*	*~2.0*	*~2.3*	*~2.1*	*~2.1*	*~2.2*
H-23b	4.88 m	4.88 m	4.89 m	4.89 m	4.85 m	4.85 m	4.85 m	4.86 m	4.84 m
H-24	1.719 m	1.723 m	1.729 m	1.733 m	1.723 m	1.725 bs	1.732 m	1.736 m	1.708 m
H-28a	3.35 dd	3.32 dd	3.53 dd	3.51 dd	3.34 bd	3.17 d	3.54 dd	3.52 dd	3.86 bd
	10.8;1.1	*10.9;1.2*	*9.3;1.5*	*9.4;1.4*	*11.0*	*8.8*	*9.2;1.6*	*9.3;1.5*	*11.2*
H-28b	3.79 dd	3.76 dd	3.64 bd	3.61 bd	3.80 bd	3.59 dd	3.63 bd	3.61 bd	4.25 dd
	10.8;1.9	*10.9;1.7*	*9.3*	*9.4*	*11.0*	*8.8;1.2*	*9.2*	*9.3*	*11.2;1.8*
H-29	4.61 m		4.59 m		4.59 m	4.59 m	4.58 m		4.61 m
		0.778 d		0.759 d				0.756 d	
H-29b	4.69 bd	*6.5*	4.68 bd	*7.0*	4.69 bd	4.68 bd	4.67 bd	*6.5*	4.70 bd
	~2.4		*~2.4*		*~2.4*	*~2.3*	*~2.4*		*~2.3*
H-30	1.690 m	0.850 d	1.674 m	0.840 d	1.688 bs	1.679 bs	1.672 m	0.836 d	1.698 m
		6.5		*7.0*				*6.5*	
OMe	–	–	–	–	3.65 s	3.65 s	3.65 s	3.66 s	–
OAc	–	–	–	–	–	–	–	–	2.074 s
					Glucose moiety				
H-1	–	–	4.46 d	4.45 d	–	5.69 d	4.46 d	4.45 d	5.71 d
			8.0	*8.0*		*5.2*	*8.0*	*8.0*	*8.2*
H-2	–	–	5.02 dd	5.01 dd	–	4.31 dd	5.02 dd	5.01 dd	5.13 dd
			9.6;8.0	*9.7;8.0*		*5.2;3.1*	*9.7;8.0*	*9.7;8.0*	*9.6;8.2*
H-3	–	–	5.22 t	5.22 t	–	5.19 t	5.22 dd	5.22 dd	5.24 t
			~9.7;9.7	*~9.7;9.7*		*3.0;3.0*	*9.7;9.4*	*9.7;9.4*	*9.4;9.4*
H-4	–	–	5.10 t	5.10 t	–	4.91 dd	5.10 dd	5.10 dd	5.13 t
			~9.7;9.7	*~9.6;9.6*		*9.6;2.9*	*9.9;9.4*	*10.0;9.4*	*9.4;9.4*
H-5	–	–	3.70 ddd	3.69 ddd	–	3.97 ddd	3.70 ddd	3.69 ddd	3.83 ddd
			9.8;4.6;2.6	*9.9;4.6;2.6*		*9.4;5.2;3.0*	*9.9;4.6;2.6*	*10.0;4.6;2.6*	*9.8;4.5;2.3*
H-6b	–	–	4.15 dd	4.14 dd	–	4.19 dd	4.15 dd	4.14 dd	4.10 dd
			12.4;2.6	*12.4;2.6*		*12.2;3.0*	*12.2;2.6*	*12.2;2.6*	*12.3;2.3*
H-6b	–	–	4.30 dd	4.29 dd	–	4.22 dd	4.30 dd	4.29 dd	4.29 dd
			12.4;4.6	*12.4;4.6*		*12.2;5.2*	*12.2;4.6*	*12.2;4.6*	*12.3;4.5*
OAc	–	–	2.014 s	2.011 s	–	2.098 s	2.013 s	2.010 s	2.006 s
			2.017 s	2.014 s		2.105 s	2.018 s	2.015 s	2.017 s
			2.030 s	2.027 s		2.121 s	2.029 s	2.026 s	2.034 s
			2.101 s	2.097 s			2.101 s	2.096 s	2.087 s

[a] Orthoacetate methyl group: 1.74 s; [b] signal was not assigned.

TABLE III

Proton NMR data of compounds **36a**, **38a**, **40a**, **41a**, **45a**, **46a** and **46b** in $CDCl_3$

Proton	Chemical shifts (*coupling constants*)						
	36a	**38a**	**40a**[a]	**41a**[a]	**45a**[b]	**46a**	**46b**
			Aglycone moiety				
CH_3	0.782 s	0.774 s	0.774 s	0.804 s	0.910 s	0.907 s	0.922 s
	0.976 s	0.987 s	0.982 s	0.991 s	1.000 s	1.000 s	0.978 s
	1.062 s	1.054 s	1.061 s	1.074 s	1.034 s	1.031 s	1.038 s
H-1a	[c]	[c]	[c]	[c]	2.25 d	2.26 d	2.29 d
					~18.0	*18.1*	*17.8*
H-1b	[c]	[c]	[c]	[c]	2.42 d	2.43 d	2.44 d
					~18.0	*18.1*	*17.8*
H-3a	3.34 dt	3.34 dt	3.34 dt	3.98 m	–	–	–
	9.2;7.1;7.1	*9.2;7.1;7.1*	*9.3;7.0;7.0*				
H-3b	3.85 ddd	3.85 ddd	3.85 ddd	3.98 m	–	–	–
	9.2;6.7;5.5	*9.2;6.8;5.4*	*9.2;6.7;5.5*				
H-19	2.36 td	2.39 td	2.45 td	2.37 td	[c]	2.36 td	[c]
	11.0;11.0;5.8	*10.8;10.8;5.8*	*11.0;11.0;5.7*	*11.0;11.0;5.7*		*10.8;10.8;5.8*	
H-23a	4.60 bd	4.60 bd	4.59 bd	4.64 bd			
	~2.2	*~2.0*	*~2.2*	*~2.2*	1.225 s	1.231 s	1.242 s
H-23b	4.82 m	4.81 m	4.81 m	4.84 m			
H-24	1.703 bs	1.692 bs	1.692 m	1.722 m	1.233 m	1.239 s	1.247 s
H-28a	3.54 bd	3.34 bd	3.86 bd	3.54 bd	3.17 bd	3.53 bdd	3.51 bd
	9.4	*11.0*	*11.0*	*9.3*	*~9.0*	*9.2;1.3*	*9.2*
H-28b	3.63 bd	3.80 dd	4.24 dd	3.63 bd	3.58 bd	3.63 bd	3.60 bd
	9.4	*11.0;1.6*	*11.0;1.5*	*9.3*	*~9.0*	*9.2*	*9.2*
H-29a	4.59 m	4.60 m	4.61 m	4.59 m	4.57 m	4.56 m	
							0.744 d
H-29b	4.67 bd	4.69 bd	4.70 bd	4.68 bd	4.67 bd	4.66 bd	*~7.0*
	~2.4	*~2.4*	*~2.4*	*~2.4*	*~2.2*	*~2.4*	
H-30	1.675 bs	1.692 bs	1.692 m	1.682 bs	1.66 bs	1.658 m	0.824 d
							~7.0
OMe	–	–	–	–	3.61 s	3.61 s	3.62 s
					3.64 s	3.64 s	3.65 s
OAc	–	–	2.073 s	2.041 s	–	–	–
			Glucose moiety				
	36a[d]	**36a**[e]					
H-1	4.47 d	4.46 d	4.47 d	4.48 d	4.47 d	5.69 d	4.45 d	4.44 d
	8.0	*8.0*	*8.0*	*8.0*	*8.0*	*5.2*	*8.0*	*8.0*
H-2	4.98 dd	5.02 dd	4.98 dd	4.98 dd	5.02 dd	4.31 dd	5.01 dd	5.00 dd
	9.7;8.0	*9.7;8.0*	*9.7;8.0*	*9.7;8.0*	*9.7;8.0*	*5.2;3.0*	*9.7;8.0*	*9.7;8.0*
H-3	5.19 t	5.22 t	5.19 dd	5.19 t	5.22 t	5.18 t	5.22 dd	5.21 t
	9.5;9.5	*9.6;9.6*	*9.7;9.5*	*9.5;9.5*	*9.6;9.6*	*3.0;3.0*	*9.7;9.4*	*9.7;9.4*
H-4	5.08 t	5.10 t	5.08 dd	5.08 dd	5.11 t	4.91 dd	5.10 dd	5.10 dd
	9.8;9.8	*9.8;9.8*	*9.9;9.5*	*9.9;9.5*	*9.7;9.7*	*9.5;2.8*	*9.9;9.4*	*9.9;9.4*
H-5	3.68 ddd	3.70 ddd	3.68 ddd	3.68 ddd	3.70 ddd	3.96 ddd	3.70 ddd	3.69 ddd
	10.0;4.6;2.5	*10.0;4.6;2.5*	*9.9;4.6;2.4*	*10.0;4.6;2.4*	*10.0;4.6;2.4*	*~10.0;5.0;3.0*	*9.9;4.6;2.6*	*9.9;4.6;2.6*
H-6a	4.13 dd	4.15 dd	4.13 dd	4.13 dd	4.15 dd	4.19 m	4.14 dd	4.14 dd
	12.4;2.5	*12.4;2.5*	*12.4;2.4*	*12.4;2.6*	*12.4;2.6*		*12.2;2.6*	*12.2;2.6*
H-6b	4.26 dd	4.30 dd	4.26 dd	4.26 dd	4.30 dd	4.22 m	4.29 dd	4.29 dd
	12.4;4.6	*12.4;4.6*	*12.4;4.6*	*12.4;4.6*	*12.4;4.6*		*12.2;4.6*	*12.2;4.6*
OAc	2.006 s	2.013 s	2.005 s	2.007 s	2.014 s	2.095 s	2.012 s	2.009 s
	2.024 s	2.018 s	2.024 s	2.025 s	2.020 s	2.101 s	2.016 s	2.012 s
	2.026 s	2.029 s	2.026 s	2.028 s	2.030 s	2.119 s	2.027 s	2.025 s
	2.086 s	2.103 s	2.085 s	2.086 s	2.103 s		2.098 s	2.093 s

[a] Data were obtained from the mixture of compounds **40a** and **41a**; [b] orthoacetate methyl group: 1.73 s; [c] signal was not assigned; [d] 3-*O*-Glc(Ac)$_4$; [e] 28-*O*-Glc(Ac)$_4$.

TABLE IV
Proton NMR data of compounds **5a**, **8a**, **11a**, **29a**, **37a** and **39a** in CD_3OD

Proton	Chemical shifts (*coupling constants*)					
	5a	**8a**	**11a**	**29a**	**37a**	**39a**
			Aglycone moiety			
CH_3	0.826 s	0.852 s	0.824 s	0.859 s	0.824 s	0.823 s
	0.868 s	0.861 s	0.865 s	1.053 s	1.045 s	1.045 s
	0.935 s	0.893 s	0.957 s	1.137 s	1.131 s	1.122 s
	1.003 s	0.967 s	1.000 s	1.747 bs	1.729 bs	1.728 bs
	1.033 s	1.014 s	1.030 s			
H-3a	3.15 dd	4.44 dd	3.15 dd	–	3.40 td	3.40 td
	11.5;4.5	*11.2;5.2*	*11.4;4.4*		*8.6;8.6;6.4*	*8.6;8.6;6.4*
H-3b	–	–	–	–	3.84 td	3.84 td
					8.6;8.6;5.4	*9.0;9.0;5.5*
H-19	2.99 td	3.01 td	3.00 td	2.47 td	2.47 td	2.43 td
	10.8;10.8;5.0	*11.0;11.0;5.0*	*10.7;10.7;4.6*	*10.8;10.8;5.5*	*10.5;10.5;5.6*	*10.6;10.6;5.6*
H-23a	[a]	[a]	[a]	4.68 bd	4.66 bd	4.66 bd
				2.4	*2.4*	*2.4*
H-23a	[a]	[a]	[a]	4.85 m	4.82 m	4.82 m
H-28a	–	–	–	3.63 dd	3.63 bd	3.29 bd
				9.5;1.5	*9.6*	*11.2*
H-28b	–	–	–	3.75 bd	3.75 bd	3.75 dd
				9.5	*9.6*	*11.2;1.6*
H-29a	4.60 m	4.60 m	4.60 m	4.59 m	4.58 m	4.59 m
H-29b	4.72 bd	4.72 bd	4.72 bd	4.70 bd	4.70 bd	4.70 bd
	2.2	*2.2*	*2.2*	*2.4*	*2.5*	*2.4*
H-30	1.694 bs	1.698 bs	1.695 bs	1.707 bs	1.703 bs	1.702 bs
OMe	3.66 s	–	–	–	–	–
OAc	–	2.02 s	–	–	–	–
			Glucose moiety			
			11a[b]	**11a**[c]	**37a**[b]	**37a**[c]
H-1	4.31 d	5.49 d	4.31 d	5.50 d	4.23 d	4.24 d	4.23 d	4.24 d
	7.8	*8.1*	*7.8*	*8.2*	*7.8*	*7.8*	*7.8*	*7.8*
H-2	3.18 dd	3.32 dd	3.18 dd	3.32 t	3.19 dd	3.17 dd	3.19 dd	3.17 dd
	8.8;7.8	*8.8;8.2*	*8.8;7.8*	*8.2;8.2*	*7.8;9.0*	*9.0;7.8*	*9.0;7.8*	*9.0;8.0*
H-3	3.33 t	3.37–3.45 m	3.33 t	3.37–3.45 m	3.36 t	3.34 t	3.36 t	3.34 t
	8.6;8.6		*8.8;8.8*		*9.0;9.0*	*8.5;8.5*	*9.0;9.0*	*8.6;8.6*
H-4	3.28 t	3.37–3.45 m	3.28 t	3.37–3.45 m	~3.28 m	3.30 t	~3.29 m	3.30 t
	9.2;9.2		*8.8;8.8*			*9.0;9.0*		*8.6;8.6*
H-5	3.23 ddd	3.37–3.45 m	3.24 ddd	3.37–3.45 m	~3.28 m	3.24 ddd	~3.29 m	3.24 ddd
	9.4;5.4;2.2		*9.4;5.4;2.4*			*9.0;5.5;2.4*		*9.0;5.5;2.4*
H-6a	3.66 dd	3.70 m	3.66 dd	3.70 m	3.69 m	3.68 dd	3.69 m	3.68 dd
	11.7;5.4		*11.6;5.4*			*11.8;5.4*		*11.8;5.5*
H-6b	3.84 dd	3.84 dd	3.835 dd	3.84 dd	3.89 dd	3.85 dd	3.89 dd	3.85 dd
	11.7;2.2	*11.8;1.6*	*11.6;2.4*	*11.8;1.5*	*11.8;2.0*	*11.8;2.4*	*11.6;1.8*	*11.8;2.4*

[a] Signal is presented in methyl groups; [b] 3-*O*-Glc; [c] 28-*O*-Glc.

TABLE V

Carbon-13 chemical shifts of compounds **4a**, **4b**, **7a**, **7b**, **10a**, **16b**, **18a**, **18b**, **20a** and **20b** in $CDCl_3$

Carbon	Chemical shifts (*coupling constants*)									
	4a	**4b**	**7a**	**7b**	**10a**	**16b**	**18a**	**18b**	**20a**	**20b**
					Aglycone moiety					
1	38.64	38.64	38.32	38.34	38.59	39.50	32.50	32.58	32.50	32.59
2	25.89	25.89	23.63	23.63	25.86	34.09	11.39	11.37	11.40	11.37
3	90.74	90.70	80.85	80.86	90.65	218.05	120.22	120.24	120.17	120.18
4	38.95	38.96	37.74	37.75	38.93	47.31	146.99	147.01	146.92	146.93
5	55.65	55.61	55.34	55.32	55.57	54.83	50.47	50.45	50.46	50.44
6	18.14	18.14	18.13	18.14	18.13	19.58	24.18	24.17	24.16	24.15
7	34.28	34.36	34.28	34.37	34.35	33.55	34.41	34.34	34.41	34.34
8	40.67	40.68	40.62	40.67	40.63	40.83	40.60	40.66	40.58	40.62
9	50.53	50.30	50.38	50.16	50.48	49.34	40.41	40.06	40.43	40.07
10	36.89	36.87	37.05	37.03	36.87	36.79	39.39	39.40	39.40	39.40
11	20.86	20.89	20.83	20.87	20.84	21.29	21.46	21.49	21.46	21.50
12	25.50	26.90	25.38	26.79	25.45	26.76	24.81	26.47	24.76	26.40
13	38.22	38.08	38.13	38.00	38.11	37.30	37.23	36.72	37.60	37.15
14	42.35	42.49	42.38	42.54	42.37	42.92	43.07	43.25	43.08	43.27
15	29.62	29.63	29.64	29.60	29.64	26.89	26.95	26.83	26.96	26.86
16	32.15	32.07	31.66	31.59	31.66	29.47	28.99	29.16	29.30	29.42
17	56.55	56.98	56.77	57.19	56.78	47.19	47.71	47.85	46.99	47.17
18	49.47	48.94	49.07	48.57	49.11	47.88	48.56	47.92	48.46	47.82
19	46.93	44.17	46.75	44.07	46.70	44.66	47.72	44.47	47.89	44.63
20	150.64	29.72	150.12	29.70	150.19	29.47	150.23	29.46	150.16	29.47
21	30.61	22.73	30.31	22.54	30.34	21.56	29.62	21.67	29.53	21.56
22	36.95	37.30	36.44	36.86	36.44	34.68	33.88	33.95	34.59	34.66
23	27.59	27.59	27.87	27.89	27.56	26.58	113.99	114.00	114.05	114.06
24	16.13	16.13	16.43	16.45	16.11	21.04	22.74	22.75	22.78	22.79
25	16.00	15.97[a]	16.13	16.10	16.00	15.84	19.74	19.68	19.72	19.65
26	15.91	15.93[a]	15.94	15.96	15.95	15.84	15.92	15.95	15.99	16.02
27	14.61	14.53[b]	14.62	14.52	14.60	14.62	14.56	14.43	14.67	14.53
28	176.66	176.88	174.22	174.51	174.15	68.64	60.44	60.51	68.49	68.60
29	109.55	22.94	109.83	22.84	109.77	22.90	109.93	22.89	109.90	22.89
30	19.39	14.67[b]	19.30	14.60	19.39	14.81	19.00	14.84	18.97	14.82
OAc	–	–	171.05	171.05	–	–	–	–	–	–
			21.28	21.29						
OMe	51.24	51.14	–	–	–	–	–	–	–	–
					Glucose moiety					
					10a[c]	**10a**[d]				
1	102.96	102.97	91.02	90.99	102.95	91.04	101.64	–	–	101.55	101.61
2	71.50	71.50	69.86	69.86	71.48	69.88	71.27	–	–	71.22	71.25
3	72.87	72.87	72.49[a]	72.46[a]	72.84	72.51[a]	72.77	–	–	72.73	72.74
4	68.79	68.76	67.95	67.97	68.74	67.96	68.59	–	–	68.54	68.57
5	71.66	71.65	72.85[a]	72.92[a]	71.62	72.84[a]	71.68	–	–	71.71	71.67
6	62.28	62.24	61.47	61.50	62.25	61.47	62.05	–	–	62.00	62.04
OAc	170.67	170.68	170.62	170.62	170.68	170.68	170.73	–	–	170.72	170.72
	170.40	170.40	170.19	170.19	170.42	170.17	170.41			170.40	170.41
	169.44	169.44	169.42	169.42	169.45	169.43	169.42			169.42	169.42
	169.18	169.18	168.97	168.95	169.19	169.00	169.20			169.18	169.18
	20.73	20.73	20.66	20.65	20.73	20.69	20.73	–	–	20.73	20.73
	20.67	20.68	20.55	20.55	20.66	20.55	20.61			20.60	20.61
	20.60	20.60	20.52	20.55	20.61	20.55	20.58			20.57	20.57
	20.58	20.58	20.52	20.52	20.59	20.55	20.58			20.57	20.57

[a,b] Signals with identical symbols may be mutually interchanged; [c] 3-*O*-Glc(Ac)$_4$; [d] 28-*O*-Glc(Ac)$_4$.

TABLE VI

Carbon-13 chemical shifts of compounds **23a**, **27a**, **27b**, **30a**, **36a**, **38a**, **40a**, **41a**, **46a** and **46b** in $CDCl_3$

Carbon	Chemical shifts (*coupling constants*)									
	23a	**27a**	**27b**	**30a**	**36a**	**38a**	**40a**[a]	**41a**[a]	**46a**	**46b**
					Aglycone moiety					
1	32.69	32.68	32.76	32.57	32.71	32.68	32.68	32.68	41.91	41.94
2	28.38	28.35	28.36	28.58	23.09	23.08	23.11	22.15	171.93	172.00
3	174.62	174.55	174.58	172.14	71.21	71.24	71.25	65.05	179.98	179.97
4	147.56	147.49	147.50	147.34	148.04	148.09	148.11	147.89	46.29	46.36
5	50.25	50.22	50.18	50.27	50.24	50.25	50.29	50.29	48.30[b]	48.32[b]
6	24.53	24.51	24.48	24.39	24.54	24.54	24.53	24.53	20.63	20.70
7	34.06	34.04	33.99	33.82	35.47	35.46	35.45	35.29	33.13	33.25
8	40.59	40.55	40.57	40.54	40.50	40.52	40.52	40.51	40.73	40.78
9	40.62	40.61	40.24	40.63	40.58	40.55	40.56	40.56	41.77[b]	41.63[b]
10	39.19	39.19	39.15	39.17	39.09	39.08	39.08	39.12	41.52	41.63
11	21.33	21.32	21.32	21.29	21.25	21.23	21.22	21.38	21.78	21.81
12	25.10	25.02	26.69	25.05	25.06	25.11	25.13	25.04	25.23	26.93
13	37.35	37.70	37.24	37.58	37.73	37.34	37.63	37.76	37.83	37.37
14	43.09	43.08	43.27	43.07	43.07	43.05	43.08	43.08	43.04	43.24
15	27.03	27.04	26.90	27.03	27.05	27.01	27.06	27.06	27.04	26.93
16	29.06	29.32	29.43	29.63[b]	29.31	29.04	29.45	29.32	29.26	29.38
17	47.75	47.03	47.18	46.28	47.04	47.74	46.28	47.06	47.08	47.24
18	48.67	48.54	47.86	48.66	48.56	48.66	48.70	48.57	48.49	47.83
19	47.73	47.88	44.63	47.65	47.90	47.72	47.65	47.92	47.89	44.59
20	150.37	150.30	29.46	150.03	150.33	150.38	150.09	150.42	150.38	29.42
21	29.69	29.58	21.54	29.54[b]	29.59	29.68	29.65	29.60	29.58	21.54
22	33.91	34.60	34.66	34.50	34.60	33.90	34.50	34.60	34.56	34.63
23	113.39	113.44	113.45	113.67	113.04	112.97	112.98	113.14	27.81	27.70
24	23.24	23.28	23.30	23.10	23.23	23.17	23.17	23.09	23.67	23.77
25	20.04	20.03	19.96	20.00	20.40	20.41	20.41	20.36	19.68	19.64
26	15.94	16.00	16.03	15.95	16.02	15.93	16.02	16.02	15.93	15.98
27	14.60	14.70	14.56	14.63	14.77	14.64	14.67	14.78	14.81	14.84
28	60.50	68.56	68.69	62.73	68.60	60.47	62.77	68.58	68.63	68.71
29	109.80	109.77	22.89	110.03	109.79	109.79	109.96	109.71	109.69	22.89
30	19.06	19.02	14.81	19.11	19.02	19.04	19.10	19.10	18.97	14.67
OAc	–	–	–	171.65	–	–	171.67	171.20	–	–
				21.02			21.03	20.98		
OMe	51.55	51.56	51.58	–	–	–	–	–	50.79	50.85
									51.72	51.72
					Glucose moiety					
					36a[d]	**36a**[e]				
1	–	101.60	101.67	91.61	101.20	101.63	101.19	101.22	101.62	101.63	101.68
2	–	71.24	71.26	70.21	71.27	71.24	71.26	71.27	71.24	71.25	71.27
3	–	72.76	72.75	72.76[c]	72.85	72.76	72.84	72.86	72.76	72.75	72.77
4	–	68.57	68.56	67.81	68.42	68.55	68.41	68.43	68.55	68.56	68.59
5	–	71.72	71.66	72.71[c]	71.77	71.71	71.75	71.77	71.71	71.70	71.66
6	–	62.02	62.03	61.47	61.97	62.02	61.95	61.97	62.02	62.02	62.04
OAc	–	170.72	170.75	170.62	170.75	170.75	170.72	170.73	170.73	170.72	170.72
		170.39	170.41	170.13	170.37	170.40	170.36	170.37	170.37	170.39	170.40
		169.42	169.43	169.40	169.42	169.42	169.42	169.43	169.43	169.42	169.42
		169.19	169.22	169.12	169.22	169.22	169.22	169.22	169.22	169.19	169.20
	–	20.73	20.73	20.67	20.74	20.72	20.70	20.72	20.72	20.73	20.73
		20.61	20.62	20.55	20.61	20.61	20.59	20.61	20.61	20.60	20.61
		20.58	20.58	20.55	20.61	20.59	20.59	20.61	20.59	20.57	20.57
		20.58	20.58	20.45	20.59	20.59	20.56	20.59	20.59	20.57	20.57

[a] Data have been obtained from the mixture of compounds **40a** and **41a**; [b,c] signals with identical symbols may be mutually interchanged; [d] 3-*O*-Glc(Ac)$_4$; [e] 28-*O*-Glc(Ac)$_4$.

(+8.1 ppm) and a small upfield shift of the C-17 signal (–0.7 ppm). Smaller shifts were observed for the more distant carbon atoms (C-13: +0.4 ppm; C-16: +0.3 ppm; C-22: +0.7 ppm). Glucosylation of the 3β-OH group results in downfield shift of C-3 (+12.1 ppm) and upfield shift of C-2 (–1.4 ppm) signals; the signal of quaternary C-4 atom is influenced only a little (+0.2), less than signals of C-5 (+0.4 ppm) and of carbon atoms in methyl groups attached in position 4 (C-23: –0.3 ppm; C-24: +0.8). In the ^{13}C NMR spectra of 3-hydroxy-3,4-seco derivatives there are significant shifts of the C-3 (+7.9 ppm) and C-2 (–2.9 ppm) signals and also signals of the more distant atoms C-6 (–0.4 ppm) and C-7 (+0.4 ppm).

Small but systematic differences occur in the chemical shifts of protons and carbon atoms of the glucose part in glucoside acetates with the sugar moiety attached in position 3 or 28. On this basis we assigned the ^{1}H and ^{13}C NMR signals for diglucoside acetates **10a** and **36a** to the individual glucose moieties in positions 3 and 28. The same principle was also applied to the isomeric glucoside acetates **40a** and **41a** (obtained only as a 1 : 1 mixture).

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Optical rotation was measured in chloroform (unless stated otherwise) on an automatic polarimeter ETL-NPL (Bendix–Ericsson) with accuracy of ±2°. Infrared spectra were recorded in chloroform on a PE 684 (Perkin–Elmer) spectrometer; wavenumbers are given in cm^{-1}. Proton and ^{13}C NMR spectra were taken on an FT spectrometer Varian UNITY-500 (^{1}H at 500 MHz, ^{13}C at 125.7 MHz) in deuteriochloroform (unless stated otherwise) with tetramethylsilane as internal standard (for the ^{13}C NMR data $\delta(CDCl_3)$ = 77.00 ppm). In the ^{13}C NMR spectra the number of directly bonded hydrogen atoms was determined from proton decoupled "attached proton test" spectra. Values of chemical shifts (δ-scale) and coupling constants (Hz) in the ^{1}H NMR spectra were obtained by first order analysis and the assignment was confirmed by H,H-COSY spectra. Proton NMR spectra of compounds **14b** and **19b** were measured at 80 MHz on an FT spectrometer Tesla BS 587A. Fast atom bombardment mass spectra (FAB-MS) were taken on a ZAB-EQ instrument (VG Analytical Ltd., Manchester), electron impact mass spectra (EI-MS) on an INCOS 50 instrument (Finnigan MAT), ionizing electron energy 70 eV.

Methyl esters were prepared by treatment of the corresponding acids with ethereal solution of diazomethane. Column chromatography was performed on silica gel Silpearl (Kavalier, Votice). Purity of the samples was checked by thin-layer chromatography (TLC) on DC-Alufolien Kieselgel 60 foils (Merck). Spots were detected by spraying with 10% sulfuric acid and subsequent heating. Preparative TLC was carried out on silica gel 60G (Merck); spots were detected with UV light (254 nm) after spraying with 0.3% solution of morin in methanol. Analytical samples were dried over phosphorus pentoxide at 100 °C under diminished pressure.

28-Acetoxy-20(29)-lupen-3-one Oxime (**14a**)

A solution of ketone[13] **13a** (9.7 g, 20 mmol) and hydroxylamine hydrochloride (7.0 g, 100 mmol) in pyridine (50 ml) was heated at 80 °C for 1 h and then set aside at room temperature overnight. The reaction mixture was poured into water, the formed precipitate was collected, washed with water, dissolved in ether and the solution was dried over sodium sulfate. Purification by chromatography on a column of silica gel in benzene–ether (10 : 1) and crystallization from chloroform–methanol af-

forded oxime **14a** (8.1 g, 81%), m.p. 203–204 °C, $[\alpha]_D$ –7.5° (*c* 0.51). Reported[16] m.p. 205–208 °C. IR spectrum: 3 586, 3 264 broad, 1 723, 1 640, 1 388, 1 367, 1 246, 919, 892.

28-Acetoxylupan-3-one Oxime (**14b**)

Using the procedure described for oxime **14a**, ketone[13] **13b** (5.0 g, 10 mmol) was converted into oxime **14b** (4.1 g, 80%), m.p. 230–233 °C (chloroform–ethanol), $[\alpha]_D$ –35° (*c* 0.52). Reported[16] m.p. 219–220 °C. IR spectrum: 3 580, 3 270b, 1 724, 1 388, 1 367, 1 249, 914. ^{1}H NMR spectrum (80 MHz): 0.76 d, 3 H, *J* = 6.5; 0.84 d, 3 H, *J* = 6.5; 0.94 s, 6 H; 1.05 s, 3 H; 1.07 s, 3 H and 1.14 s, 3 H (7 × CH_3); 2.05 s, 3 H (CH_3COO); 2.23 ddd, 1 H, *J* = 15.5; 11.5 and 5.5 (H-2β); 3.00 ddd, 1 H, *J* = 15.5, 5.5 and 3.5 (H-2α); 3.82 d, 1 H, *J* = 11 (H-28a); 4.26 d, 1 H, *J* = 11 (H-28b). EI-MS, *m/z* (%): 499 (M^+, 19), 482 (67), 426 (10), 422 (12), 398 (20), 357 (20), 235 (68), 191 (37), 43 (100).

28-Hydroxy-3,4-secolupa-4(23),20(29)-diene-3-nitrile (**18a**)

Nitrile **19a** (190 mg, 0.4 mmol) was hydrolyzed by treatment with 2.5% solution of potassium hydroxide in benzene–ethanol (1 : 1; 8 ml) at room temperature for three days. The reaction mixture was dissolved in ether, washed with water and the ethereal solution was dried over sodium sulfate. Evaporation of the solvent gave the nitrile **18a** (160 mg, 92%), m.p. 115–117 °C (ether–light petroleum), $[\alpha]_D$ +37° (*c* 0.47). IR spectrum: 3 624, 3 071, 2 243, 1 638, 893. EI-MS, *m/z* (%): 437 (M^+, 32), 419 (15), 406 (100), 283 (32), 189 (39). For $C_{30}H_{47}NO$ (437.7) calculated: 82.32% C, 10.82% H, 3.20% N; found: 82.06% C, 10.64% H, 3.52% N.

28-Hydroxy-3,4-secolup-4(23)-ene-3-nitrile (**18b**)

Using the procedure described for nitrile **18a**, nitrile **19b** (200 mg, 0.4 mmol) was converted into nitrile **18b** (160 mg, 88%), m.p. 157–159 °C (ether), $[\alpha]_D$ –5° (*c* 0.50). IR spectrum: 3 625, 3 071, 2 245, 1 633, 898. EI-MS, *m/z* (%): 439 (M^+, 9), 424 (4.5), 421 (5), 408 (100), 191 (43). For $C_{30}H_{49}NO$ (439.7) calculated: 81.94% C, 11.23% H, 3.19% N; found: 81.71% C, 10.99% H, 3.48% N.

28-Acetoxy-3,4-secolupa-4(23),20(29)-diene-3-nitrile (**19a**)

A solution of oxime **14a** (8.0 g, 16.2 mmol) and 4-toluenesulfonyl chloride (18 g, 94 mmol) in pyridine (150 ml) was refluxed for 3 h. After cooling, the reaction mixture was poured into water, the precipitate was collected, washed with water and dissolved in chloroform. The solution was dried by filtration through a layer of silica gel and the product was crystallized from chloroform–methanol to give nitrile **19a** (6.6 g, 85%), m.p. 121–122 °C, $[\alpha]_D$ +24° (*c* 0.49). Reported[16] m.p. 120–122 °C. IR spectrum: 3 070, 2 247, 1 722, 1 632, 1 242, 895. EI-MS, *m/z* (%): 479 (M^+, 34), 419 (21), 406 (27), 376 (18), 338 (16), 203 (62), 189 (33), 43 (100).

28-Acetoxy-3,4-secolup-4(23)-ene-3-nitrile (**19b**)

Using the procedure described for nitrile **19a**, oxime **14b** (4.7 g, 9.5 mmol) was converted into amorphous nitrile **19b** (3.9 g, 86%), $[\alpha]_D$ –8° (*c* 0.54). IR spectrum: 3 071, 2 244, 1 724, 1 633, 1 247, 900. ^{1}H NMR spectrum (80 MHz): 0.78 d, 3 H, *J* = 6.5; 0.85 d, 3 H, *J* = 6.5; 0.85 s, 3 H; 0.97 s, 3 H, and 1.09 s, 3 H (5 × CH_3); 1.72 bs, 3 H (3 × H-24); 2.05 s, 3 H (CH_3COO); 2.14–2.46 m, 2 H (2 × H-2); 3.83 d, 1 H, *J* = 11 (H-28a); 4.26 dd, 1 H, *J* = 11 and 1 (H-28b); 4.65 bd, 1 H, *J* = 2 (H-23a); 4.88 m, 1 H (H-23b). EI-MS, *m/z* (%): 481 (M^+, 15), 421 (14), 408 (23), 378 (6), 340 (13), 289 (10), 229 (15), 203 (20), 191 (57), 43 (100).

28-Hydroxy-3,4-secolupa-4(23),20(29)-dien-3-oic Acid (**22a**)

A solution of nitrile **19a** (6.0 g, 12.5 mmol) and sodium hydroxide (15 g, 0.4 mol) in ethylene glycol (150 ml) was refluxed for 6 h. After cooling, the reaction mixture was poured into an excess of dilute hydrochloric acid (1 : 4), the precipitate was collected, washed with water till neutral reaction of the washings, dissolved in ether and the solution was dried over sodium sulfate. Repeated crystallization from chloroform–heptane afforded acid **22a** (4.7 g, 82%), m.p. 136–162 °C (decomp.), $[\alpha]_D$ +36° (*c* 0.47). IR spectrum: 3 514, 3 300–2 600, 3 071, 1 707, 1 640, 894. EI-MS, *m/z* (%): 456 (M^+,17), 425 (25), 383 (26), 375 (23), 357 (60), 345 (41), 81 (100).

Methyl ester **23a**: m.p. 171–173 °C (ether–light petroleum), $[\alpha]_D$ +33° (*c* 0.38). IR spectrum: 3 621, 3 071, 1 728, 1 638, 1 438, 895. EI-MS, *m/z* (%): 470 (M^+, 16), 439 (15), 389 (12), 383 (55), 371 (42), 359 (52), 189 (42), 81 (100). For $C_{31}H_{50}O_3$ (470.7) calculated: 79.10% C, 10.71% H; found: 79.18% C, 10.98% H.

28-Hydroxy-3,4-secolup-4(23)-en-3-oic Acid (**22b**)

Using the procedure described for acid **22a**, nitrile **19b** (3.1 g, 6.5 mmol) was converted into acid **22b** (2.7 g, 91%), m.p. 137–165 °C (decomp.) (ether–light petroleum), $[\alpha]_D$ –3° (*c* 0.49). IR spectrum: 3 621, 3 300–2 700, 1 705, 1 638, 895. EI-MS, *m/z* (%): 458 (M^+,23), 427 (37), 385 (34), 359 (100), 347 (22), 303 (13).

Methyl ester **23b**: m.p. 166–168 °C (ether), $[\alpha]_D$ –5° (*c* 0.59). Reported[17] m.p. 122 °C (ethyl acetate). IR spectrum: 3 621, 1 729, 1 638, 1 443, 895. EI-MS, *m/z* (%): 472 (29), 441 (24), 385 (88), 373 (85), 361 (68), 191 (65), 189 (42), 109 (100). For $C_{31}H_{52}O_3$ (472.8) calculated: 78.76% C, 11.09% H; found: 79.02% C, 11.23% H.

28-Acetoxy-3,4-secolupa-4(23),20(29)-dien-3-oic Acid (**24a**)

Hydroxy acid **22a** (350 mg, 77 mmol) was acetylated with acetic anhydride–pyridine mixture (3 : 2, 5 ml) at room temperature overnight. The reaction mixture was decomposed with excess of water, the product was taken up in ether, the ethereal solution was washed with dilute hydrochloric acid, 5% solution of sodium hydrogen carbonate and with water and dried over sodium sulfate. Crystallization from chloroform–heptane afforded acid **24a** (310 mg, 81%), m.p. 227–230 °C, $[\alpha]_D$ +26° (*c* 0.45). IR spectrum: 3 514, 3 071, 3 300–2 600, 1 729, 1 709, 1 640, 894. EI-MS, *m/z* (%): 498 (M^+, 8), 438 (5), 425 (22), 357 (62), 187 (25), 189 (24), 43 (100). For $C_{32}H_{50}O_4$ (498.8) calculated: 77.06% C, 10.10% H; found: 77.22% C, 10.21% H.

Methyl ester **25a**: amorphous, $[\alpha]_D$ +23° (*c* 0.56). IR spectrum: 3 071, 1 728, 1 640, 1 437, 1 246, 892. EI-MS, *m/z* (%): 512 (M^+, 16), 431 (5), 425 (31), 371 (86), 201 (30), 187 (38), 43 (100).

28-Acetoxy-3,4-secolup-4(23)-en-3-oic Acid (**24b**)

Using the procedure described for acid **24a**, acid **22b** (100 mg, 22 mmol) was converted into acid **24b** (100 mg, 92%), m.p. 199–201 °C (ether), $[\alpha]_D$ –6° (*c* 0.69). IR spectrum: 3 509, 3 069, 3 300–2 600, 1 730, 1 708, 1 636, 1 246, 897. EI-MS, *m/z* (%): 500 (M^+, 23), 440 (10), 427 (52), 367 (23), 359 (28), 191 (15), 43 (100). For $C_{32}H_{52}O_4$ (500.8) calculated: 76.75% C, 10.47% H; found: 76.54% C, 10.52% H.

Methyl ester **25b**: amorphous, $[\alpha]_D$ –7° (*c* 0.57). IR spectrum: 1 730, 1 634, 1 437, 1 245, 897. EI-MS, *m/z* (%): 514 (M^+, 4), 454 (1.5), 441 (2.5), 427 (9), 373 (38), 191 (21), 43 (100).

3,4-Secolupa-4(23),20(29)-diene-3,28-diol (**32a**)

A mixture of methyl ester **23a** (650 mg, 1.4 mmol) and lithium aluminium hydride (500 mg, 13.2 mmol) in ether (200 ml) was refluxed for 1 h. The reaction mixture was then decomposed with ethyl acetate, water and dilute sulfuric acid. The ethereal layer was washed with brine and dried over sodium sulfate. The solvent was evaporated and the residue was crystallized from ether–light petroleum to give diol **32a** (550 mg, 90%), m.p. 212–213 °C, $[\alpha]_D$ +47° (*c* 0.49). Reported[18] m.p. 212–213 °C, $[\alpha]_D$ +45° (methanol). IR spectrum: 3 623, 1 637, 893. EI-MS, *m/z* (%): 442 (M^+, 27), 411 (11), 383 (24), 361 (25), 343 (50), 331 (41), 201 (50), 85 (100).

Diacetate **33a** was prepared by acetylation of diol **32a** (100 mg, 0.22 mmol) according to the procedure described for the 28-acetoxy acid **24a**. Chromatographic purification of the crude product afforded amorphous diacetate **33a** (100 mg, 83%), $[\alpha]_D$ +30° (*c* 0.37). IR spectrum: 1 724, 1 249. EI-MS, *m/z* (%): 526 (M^+, 5), 466 (2), 453 (2), 445 (2), 425 (7), 385 (35), 325 (12), 43 (100). Ref.[19] reports only the ^{13}C NMR spectrum.

Treatment of diol **32a** (530 mg, 1.2 mmol) with acetic anhydride (0.6 ml, 6.3 mmol) in pyridine (15 ml) at –30 °C for 4 h, followed by the above-described workup, afforded a mixture of products which on chromatographic separation afforded: diacetate **33a** (80 mg, 13%), the starting diol **32a** (350 mg, 66%) and a chromatographically unseparable mixture of monoacetates **34a** and **35a** (1:1 according to ^1H NMR spectrum; 90 mg, 18%). EI-MS of the mixture, *m/z* (%): 484 (M^+, 25), 453 (14, corresponds to isomer **34a**), 425 (11, **35a**), 424 (5), 403 (12), 411 (5, **35a**), 385 (49), 383 (100, **34a**), 343 (66).

General Procedure for Preparation of Tetra-*O*-acetyl-β-D-glucopyranosyl Derivatives

A. In acetonitrile in the presence of mercury(II) cyanide: A mixture of the aglycone, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (further only acetobromoglucose) and mercury(II) cyanide in anhydrous acetonitrile (or its mixture with ether or chloroform) was refluxed. The amount of the starting aglycone was followed by TLC and, as required, further acetobromoglucose and mercury(II) cyanide was added. After completion of the reaction, the reaction mixture was diluted with ether, the ethereal solution was washed with water and dried over sodium sulfate. The solvent was evaporated and the residue subjected to preparative TLC in light petroleum–ether (1 : 1 to 2 : 3, according to polarity of the compounds separated).

B. In dichloromethane in the presence of silver silicate: A solution of acetobromoglucose in dichloromethane was added under argon to a mixture of the aglycone, silver silicate and calcined molecular sieve (4 Å) in dichloromethane. The reaction mixture was stirred in the dark at room temperature for 24 h and then without work-up subjected to column chromatography on silica gel in toluene–ether (4 : 1).

Methyl 3β-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-lup-20(29)-en-28-oate (**4a**)

A mixture of hydroxy derivative **2a** (200 mg, 0.4 mmol), acetobromoglucose (650 mg, 1.6 mmol), mercury(II) cyanide (215 mg, 0.9 mmol) and acetonitrile (10 ml) was refluxed for 34 h to give glucoside acetate **4a** (180 mg, 53%), m.p. 120–123 °C (ether–light petroleum), $[\alpha]_D$ 0° (*c* 0.56). IR spectrum: 1 754, 1 740, 1 720, 1 640, 1 433, 1 222, 909. EI-MS, *m/z* (%): 800 (M^+, 0.3), 741 (0.3), 740 (0.3), 537 (9), 469 (4), 453 (5), 393 (13), 331 (20), 189 (61), 169 (98), 109 (96), 43 (100). For $C_{45}H_{68}O_{12}$ (801.0) calculated: 67.48% C, 8.56% H; found: 67.28% C, 8.69% H. Substantial amount of the starting hydroxy derivative **2a** (50 mg, 25%) was recovered.

Methyl 3β-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-lupan-28-oate (**4b**)

A mixture of hydroxy derivative **2b** (200 mg, 0.4 mmol), acetobromoglucose (650 mg, 1.6 mmol), mercury(II) cyanide (215 mg, 0.9 mmol), acetonitrile (10 ml) and anhydrous chloroform (8 ml) was refluxed for 36 h. The reaction gave glucoside acetate **4b** (95 mg, 28%), m.p. 122–126 °C (chloroform–methanol), $[\alpha]_D$ –16° (*c* 0.71). IR spectrum: 1 753, 1 740, 1 720, 1 433, 1 225. EI-MS, *m/z*(%): 802 (M^+, 0.01), 743 (1), 537 (4), 472 (4), 470 (5), 455 (78), 411 (12), 395 (25), 331 (15), 275 (12), 271 (4), 189 (52), 169 (72), 109 (90), 43 (100). For $C_{45}H_{70}O_{12}$ (803.1) calculated: 67.31% C, 8.79% H; found: 67.15% C, 8.52% H. Great amount of the starting compound **2b** (120 mg, 60%) was recovered.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl 3β-Acetoxy-lup-20(29)-en-28-oate (**7a**)

A mixture of acid **3a** (200 mg, 0.4 mmol), acetobromoglucose (420 mg, 1 mmol), mercury(II) cyanide (250 mg, 1 mmol), acetonitrile (10 ml) and anhydrous ether (7 ml) was refluxed for 12.5 h. The reaction afforded amorphous derivative **7a** (200 mg, 60%). $[\alpha]_D$ +18° (*c* 0.55). IR spectrum: 1 754, 1 744, 1 720, 1 641, 902. EI-MS, *m/z* (%): 828 (M^+, 0.1), 768 (0.2), 725 (0.1), 331 (66), 271 (15), 189 (12), 169 (100), 109 (37), 43 (95).

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl 3β-Acetoxylupan-28-oate (**7b**)

A mixture of acid **3b** (200 mg, 0.4 mmol), acetobromoglucose (550 mg, 1.3 mmol), mercury(II) cyanide (150 mg, 0.6 mmol), acetonitrile (10 ml) and anhydrous ether (10 ml) was refluxed for 16 h. The reaction afforded amorphous derivative **7b** (78 mg, 24%). $[\alpha]_D$ +1° (*c* 0.67). IR spectrum: 1 755, 1 745, 1 722, 1 252. EI-MS, *m/z*(%): 830 (M^+, 0.1), 770 (1), 755 (0.4), 727 (0.3), 455 (3), 439 (3), 411 (1), 395 (4), 331 (72), 271 (19), 189 (19), 169 (100), 109 (42), 43 (73). Substantial amount of the starting acid **3b** (80 mg, 40%) was recovered.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl 3β-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-lup-20(29)-en-28-oate (**10a**)

A mixture of acid **1a** (200 mg, 0.4 mmol), acetobromoglucose (650 mg, 1.6 mmol), mercury(II) cyanide (405 mg, 1.6 mmol), acetonitrile (20 ml), anhydrous ether (8 ml) and anhydrous chloroform (5 ml) was refluxed for 19 h to afford derivative **10a** (40 mg, 8%), m.p. 225–231 °C (dichloromethane–ether), $[\alpha]_D$ +1° (*c* 0.46). IR spectrum: 1 755 broad, 1 642, 1 218, 908. EI-MS, *m/z* (%): 785 (M^+ –331, 0.1), 769 (0.1), 537 (0.1), 331 (28), 271 (10), 169 (100), 109 (41), 43 (49). For $C_{58}H_{84}O_{21}$ (1117.3) calculated: 62.35% C, 7.58% H; found: 62.15% C, 7.22% H. Great amount of the starting acid **1a** (150 mg, 75%) was recovered.

28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)lup-20(29)-en-3-one (**16a**)

Reaction of hydroxy derivative **12a** (220 mg, 0.5 mmol), acetobromoglucose (600 mg, 1.5 mmol), molecular sieve (800 mg) and silver silicate (500 mg) in dichloromethane (20 ml) afforded amorphous orthoacetate **15a** (120 mg, 31%) which on attempted purification decomposed to give hydroxy derivative **12a** and two tetra-*O*-acetyl derivatives of glucose (according to TLC). Also isolated was glucoside acetate **16a** (50 mg, 13%), m.p. 130–131 °C (ether–heptane), $[\alpha]_D$ +7° (*c* 0.34). IR spectrum: 1 755, 1 740, 1 698, 1 638, 1 218, 908. EI-MS, *m/z* (%): 770 (M^+, 0.3), 451 (0.3), 409 (10), 331 (44), 271 (10), 169 (100), 109 (40), 43 (53). For $C_{44}H_{66}O_{11}$ (771.0) calculated: 68.55% C, 8.64% H; found: 68.60% C, 8.48% H.

28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)lupan-3-one (**16b**)

A mixture of hydroxy derivative **12b** (50 mg, 0.1 mmol), acetobromoglucose (110 mg, 0.3 mmol), mercury(II) cyanide (30 mg, 0.12 mmol) and acetonitrile (5 ml) was refluxed for 12 h. The reaction afforded glucoside acetate **16b** (45 mg, 52%), m.p. 173.5–175 °C (ether–light petroleum), $[\alpha]_D$ –6° (*c* 0.56). IR spectrum: 1 754, 1 740, 1 698, 1 224. EI-MS, *m/z* (%): 772 (M, 0.2), 540 (0.4), 480 (0.4), 453 (0.6), 440 (0.6), 411 (18), 331 (52), 169 (100), 109 (49), 43 (85). For $C_{44}H_{68}O_{11}$ (773.0) calculated: 68.37% C, 8.87% H; found: 68.58% C, 9.03% H.

28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,4-seco-lupa-4(23),20(29)-diene-3-nitrile (**20a**)

A mixture of hydroxy derivative **18a** (150 ml, 0.3 mmol), acetobromoglucose (420 mg, 1 mmol), mercury(II) cyanide (260 mg, 1 mmol) and acetonitrile (10 ml) was refluxed for 10 h. The reaction afforded glucoside acetate **20a** (172 mg, 65%), m.p. 182–184 °C (methanol), $[\alpha]_D$ +2° (*c* 0.57). IR spectrum: 3 068, 2 247, 1 754 broad, 1 639, 1 219, 895. EI-MS, *m/z* (%): 767 (M^+, 5), 465 (0.6), 448 (0.6), 419 (11), 406 (21), 331 (49), 271 (14), 169 (100), 109 (42), 43 (53). For $C_{44}H_{65}NO_{10}$ (768.0) calculated: 68.81% C, 8.53% H; found: 68.52% C, 8.40% H.

28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,4-secolup-4(23)-ene-3-nitrile (**20b**)

A mixture of hydroxy derivative **18b** (130 mg, 0.3 mmol), acetobromoglucose (375 mg, 0.9 mmol), mercury(II) cyanide (225 mg, 0.9 mmol) and acetonitrile (10 ml) was refluxed for 10 h to give glucoside acetate **20b** (140 mg, 62%), m.p. 198–202 °C (chloroform–methanol), $[\alpha]_D$ –2° (*c* 0.52). IR spectrum: 2 247, 1 754b, 1 634, 1 218, 899. EI-MS, *m/z* (%): 769 (M^+, 2), 577 (0.3), 450 (0.1), 422 (10), 408 (23), 331 (66), 271 (12), 169 (100), 109 (48), 43 (56). For $C_{44}H_{67}NO_{10}$ (770.0) calculated: 68.63% C, 8.77% H; found: 68.20% C, 8.59% H.

Methyl 28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-dien-3-oate (**27a**)

A) A mixture of hydroxy derivative **23a** (200 mg, 0.4 mmol), acetobromoglucose (265 mg, 0.6 mmol), mercury(II) cyanide (165 mg, 0.7 mmol) and acetonitrile (10 ml) was refluxed for 7 h. The reaction afforded amorphous glucoside acetate **27a** (220 mg, 65%), $[\alpha]_D$ +5° (*c* 0.49). IR spectrum: 1 754, 1 740, 1 635, 1 436, 1 227, 898. EI-MS, *m/z* (%): 800 (M^+, 0.1), 452 (3), 439 (4), 371 (6), 169 (100), 109 (37), 43 (51). The reaction further afforded compound **25a** (30 mg, 14%), identical with an authentic sample.

B) Reaction of a mixture of hydroxy derivative **23a** (400 mg, 0.8 mmol), molecular sieve (1 g), silver silicate (650 mg) and acetobromoglucose (700 mg, 1.7 mmol) in dichloromethane (15 ml) afforded orthoacetate **26a** (200 mg, 29%) and amorphous glucoside acetate **27a** (90 mg, 13%), identical with the compound prepared by procedure *A*.

Orthoacetate **26a**: m.p. 100–102 °C (heptane), $[\alpha]_D$ +29° (*c* 0.49). IR spectrum: 1 746, 1 640, 1 435, 1 221, 893. For ^{1}H NMR spectrum see Table II. After standing for 2 days in chloroform at room temperature, the orthoacetate **26a** decomposed to give a mixture which, according to the ^{1}H a ^{13}C NMR spectra displayed signals of the hydroxy derivative **23a** (see Tables II and VI), 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose in the ratio 3 : 2 : 1.

1,3,4,6-Tetra-O-acetyl-α-D-glucopyranose: ^{1}H NMR spectrum (500 MHz): 2.053 s, 3 H; 2.087 s, 3 H; 2.109 s, 3 H and 2.208 s, 3 H (4 × CH_3); 3.66 d, 1 H, *J* = 9 (OH); 3.90 ddd, 1 H, *J* = 10, 9 and 4 (H-2); 4.03 ddd, 1 H, *J* = 10, 4 and 2 (H-5); 4.06 dd, 1 H, *J* = 12.5 and 2 (H-6a); 4.29 dd, 1 H, *J* = 12.5 and 4 (H-6b); 5.11 t, 1 H, *J* = 10 and 10 (H-4); 5.27 t, 1 H, *J* = 10 and 10 (H-3); 6.24 d, 1 H, *J* = 4 (H-1). ^{13}C NMR spectrum: 20.5–20.9 (4 × CH_3), 61.57 (C-6), 67.35 (C-4), 69.66 (C-5), 69.89 (C-2), 73.19 (C-3), 91.32 (C-1), 169–172 (4 × C=O).

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranose: ^{1}H NMR spectrum (500 MHz): 2.025 s, 3 H; 2.042 s, 3 H; 2.093 s, 3 H and 2.104 s, 3 H (4 × CH_3); 3.05 dd, 1 H, *J* = 4 and 1 (OH); 4.13 m, 1H (H-6a); 4.23–4.25 m, 2 H (H-5 and H-6b); 4.92 ddd, 1 H, *J* = 10, 4 and 1 (H-2); 5.10 t, 1 H, *J* = 10 and 10 (H-4); 5.54 t, 1 H, *J* = 10 and 10 (H-3); 5.48 t, 1 H, *J* = 4 and 4 (H-1). ^{13}C NMR spectrum: 20.5–20.9 (4 × CH_3), 61.90 (C-6), 67.29 (C-5), 68.44 (C-4), 69.81 (C-3), 71.01 (C-2), 90.21 (C-1), 169-172 (4 × C=O).

Methyl 28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,4-secolup-4(23)-en-3-oate (**27b**)

A mixture of hydroxy derivative **23b** (200 mg, 0.4 mmol), acetobromoglucose (355 mg, 0.9 mmol), mercury(II) cyanide (225 mg, 0.9 mmol) and acetonitrile (10 ml) was refluxed for 7 h. The reaction afforded glucoside acetate **27b** (230 mg, 68%), m.p. 165–166 °C (methanol), $[\alpha]_D$ –10° (*c* 0.57). IR spectrum: 1 507b, 1 635, 1 436, 1 227, 898. EI-MS, *m/z* (%): 802 (M^+, 0.5), 770 (0.2), 715 (0.5), 577 (0.3), 471 (1), 441 (2), 373 (20), 331 (100), 271 (19), 169 (89), 109 (42), 43 (55). For $C_{45}H_{70}O_{12}$ (803.1) calculated: 67.31% C, 8.79% H; found: 66.95% C, 8.53% H.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl 28-Acetoxy-3,4-secolupa-4(23),20(29)-dien-3-oate (**30a**)

A mixture of acid **24a** (220 mg, 0.4 mmol), acetobromoglucose (545 mg, 1.3 mmol), mercury(II) cyanide (225 mg, 0.9 mmol) and acetonitrile (10 ml) was refluxed for 26 h. The reaction afforded amorphous derivative **30a** (180 mg, 49%), $[\alpha]_D$ +12° (*c* 0.55). IR spectrum: 1 758, 1 740, 1 722, 1 639, 1 226, 895. EI-MS, *m/z* (%): 828 (M^+, 0.01), 768 (0.01), 755 (0.01), 497 (0.3), 481 (0.9), 437 (0.5), 425 (0.5), 421 (1.3), 357 (0.9), 331 (45), 271 (12), 169 (100), 109 (61), 43 (52). Part of the starting acid **24a** (90 mg, 41%) was recovered.

3,28-Bis(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-diene (**36a**) and 3-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-dien-28-ol (**38a**)

A mixture of diol **32a** (200 mg, 0.5 mmol), acetobromoglucose (560 mg, 1.4 mmol), mercury(II) cyanide (350 mg, 1.4 mmol) and acetonitrile (20 ml) was refluxed for 7 h. The reaction afforded amorphous glucoside acetate **38a** (70 mg, 20%). $[\alpha]_D$ +8° (*c* 0.94). IR spectrum: 3 624, 1 753, 1 742, 1 638, 1 226, 892. EI-MS, *m/z* (%): 772 (M^+, 0.5), 741 (0.5), 691 (0.4), 673 (2), 661 (2), 643 (0.4), 511 (0.4), 383 (10), 331 (71), 271 (18), 170 (76), 169 (43), 109 (81), 43 (100).

Further isolated product was derivative **36a** (300 mg, 60%), m.p. 225–227 °C (methanol), $[\alpha]_D$ –6° (*c* 0.48). IR spectrum: 1 754, 1 740, 1 639, 1 219, 892. EI-MS, *m/z* (%): 772 (M^+ – 330, 0.1), 754 (0.2), 741 (0.6), 713 (0.2), 673 (0.7), 643 (0.2), 511 (0.1), 423 (0.6), 383 (0.5), 365 (0.7), 331 (61), 271 (18), 169 (100), 109 (39), 43 (37). For $C_{58}H_{86}O_{20}$ (1103.3) calculated: 63.14% C, 7.86% H; found: 62.88% C, 7.64% H.

Also isolated was a mixture of isomeric glucoside acetates **40a** and **41a** (45 mg, 12%). EI-MS of the mixture, *m/z* (%): 814 (M^+, 1), 754 (0.2), 741 (0.2, isomer **40a**), 733 (0.2), 713 (0.2, **41a**), 673 (1), 453 (4, **41a**), 425 (4, **40a**), 331 (82), 169 (100), 109 (39), 43 (68).

Dimethyl 28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2,3-secolup-20(29)-ene-2,3-dioate (**46a**)

A) A mixture of hydroxy derivative **43a** (200 mg, 0.4 mmol), acetobromoglucose (410 mg, 1 mmol), mercury(II) cyanide (200 mg, 0.8 mmol) and acetonitrile (10 ml) was refluxed for 16 h. The reaction afforded glucoside acetate **46a** (140 mg, 43%), m.p. 169–171 °C (methanol), $[\alpha]_D$ –1° (*c* 0.46). IR spectrum: 1 753, 1 740, 1 720, 1 639, 1 433, 1 227, 888. EI-MS, *m/z* (%): 846 (M^+, 0.2), 815 (0.1), 787 (0.25), 772 (0.3), 745 (0.2), 671 (0.5), 577 (0.4), 515 (0.3), 331 (70), 271 (10), 169 (100),

109 (32), 43 (53). For $C_{46}H_{70}O_{14}$ (847.1) calculated: 65.23% C, 8.33% H; found: 65.02% C, 8.13% H. As a side product was isolated acetate **44a** (40 mg, 18%), identical with an authentic[13] sample. Also a part of the starting hydroxy derivative **43a** (60 mg, 30%) was recovered.

B) Reaction of hydroxy derivative **43a** (300 mg, 0.6 mmol) with acetobromoglucose (600 mg, 1.5 mmol) in the presence of silver silicate (700 mg) and a molecular sieve (1 g) v dichloromethane (20 ml) afforded orthoacetate **45a** (160 mg, 33%), m.p. 145–148 °C (ether), $[\alpha]_D$ +13° (*c* 1.05). IR spectrum: 1 720, 1 639, 1 433, 1 224, 888. For the ^{1}H NMR spectrum see Table III. In chloroform solution, ortho acetate **45a** decomposed to give a mixture of hydroxy derivative **43a** and two tetra-*O*-acetyl derivatives of glucose (according to TLC). Further isolated product was the glucoside acetate **46a** (105 mg, 21 %), identical with the sample prepared according to procedure *A*.

Dimethyl 28-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2,3-secolupane-2,3-dioate (**46b**)

A) A mixture of hydroxy derivative **43b** (210 mg, 0.4 mmol), acetobromoglucose (420 mg, 1 mmol), mercury(II) cyanide (200 mg, 0.8 mmol) and acetonitrile (10 ml) was refluxed for 16 h. The reaction afforded glucoside acetate **46b** (150 mg, 44%), m.p. 190–194 °C (chloroform–methanol), $[\alpha]_D$ –18° (*c* 0.53). IR spectrum: 1 753, 1 740, 1 720, 1 434, 1 227, 908. EI-MS, *m/z* (%): 848 (M^+, 0.1), 818 (0.5), 774 (0.2), 715 (0.3), 673 (0.2), 577 (0.3), 517 (0.3), 331 (87), 271 (13), 169 (100), 109 (30), 43 (42). For $C_{46}H_{72}O_{14}$ (849.1) calculated: 65.07% C, 8.55% H; found: 64.85% C, 8.60% H.

Further isolated product was the acetate **44b** (7 mg, 3%), identical with an authentic sample[13]. Also a part of the starting hydroxy derivative **43b** (85 mg, 43%) was recovered.

B) Reaction of hydroxy derivative **43b** (300 mg, 0.6 mmol) with acetobromoglucose (600 mg, 1.5 mmol) in the presence of silver silicate (700 mg) and a molecular sieve (1 g) in dichloromethane (20 ml) afforded orthoacetate **45b** (290 mg, 59%), m.p. 83–90/150–153 °C (ether), $[\alpha]_D$ –15° (*c* 0.52). IR spectrum: 1 720, 1 435, 1 222. In chloroform solution, orthoacetate **45b** decomposed to give a mixture of hydroxy derivative **43b** and two tetra-*O*-acetylderivatives of glucose (TLC).

General Procedure for Deacetylation of Tetra-*O*-acetyl-β-D-glucopyranosyl Derivatives

The glucoside acetate was dissolved in anhydrous methanol (2–6 ml, according to the amount and solubility of the compound), 5% methanolic solution of sodium methoxide (0.1–0.2 ml) was added and the solution was set aside at room temperature. The reaction time ranged from 1 to 3 h and the reaction was monitored by TLC. If the glucoside acetate was insoluble in methanol, the reaction mixture was stirred until the acetate dissolved. The work-up consisted in neutralization of the reaction mixture with 10% acetic acid and evaporation at 30 °C under diminished pressure. The residue was purified by preparative TLC in chloroform–methanol (9 : 1).

Methyl 3β-(β-D-Glucopyranosyloxy)-lup-20(29)-en-28-oate (**5a**)

Using the general procedure, glucoside acetate **4a** (120 mg, 0.15 mmol) was converted into glucoside **5a** (70 mg, 74%), m.p. 197–200/248–250 °C (methanol), $[\alpha]_D$ –3° (*c* 0.66, methanol). FAB-MS, *m/z*: 655 (M + Na), 633 (M + H), 471, 453, 393.

Methyl 3β-(β-D-Glucopyranosyloxy)lupan-28-oate (**5b**)

Glucoside acetate **4b** (21 mg, 0.03 mmol) was converted into glucoside **5b** (14 mg, 84%), m.p. 265–269 °C (chloroform–methanol), $[\alpha]_D$ –21° (*c* 0.38, methanol). FAB-MS, *m/z*: 657 (M + Na), 635 (M + H), 473, 455, 395.

β-D-Glucopyranosyl 3β-Acetoxylup-20(29)-en-28-oate (**8a**)

Glucoside acetate **7a** (170 mg, 0.21 mmol) was converted into amorphous glucoside **8a** (110 mg, 81%), $[\alpha]_D$ +4° (*c* 0.59, methanol). FAB-MS, *m/z*: 683 (M + Na), 499, 453, 439, 393.

β-D-Glucopyranosyl 3β-Acetoxylupan-28-oate (**8b**)

Glucoside acetate **7b** (85 mg, 0.09 mmol) was converted into amorphous glucoside **8b** (58 mg, 86%), $[\alpha]_D$ –13° (*c* 0.53, methanol). FAB-MS, *m/z*: 685 (M + Na), 501, 455, 441, 395.

β-D-Glucopyranosyl 3β-Hydroxylup-20(29)-en-28-oate (**9a**)

Acetate **8a** (20 mg, 0.03 mmol) was dissolved in a 1.5% solution of sodium hydroxide (0.75 mmol) in methanol (2 ml) and the solution was warmed to 50 °C for 30 min. After cooling, the reaction mixture was applied onto a preparative TLC plate and chromatographed in chloroform–methanol (9 : 1). Yield 15 mg (80%) of amorphous glucoside **9a**, $[\alpha]_D$ 0° (*c* 0.16, methanol); reported[26] m.p. 213–216 °C, $[\alpha]_D$ –2° (ethanol). FAB-MS, *m/z*: 641 (M + Na), 619 (M + H), 601, 457, 439, 411, 393.

β-D-Glucopyranosyl 3β-Hydroxylupan-28-oate (**9b**)

Using the same procedure and the same chromatography conditions as described for the preparation of glucoside **9a**, conversion of acetate **8b** (20 mg, 0.03 mmol) afforded glucoside **9b** (17 mg, 91%), m.p. 243–244 °C (methanol), $[\alpha]_D$ –21° (*c* 0.17, methanol). FAB-MS, *m/z*: 643 (M + Na), 621 (M + H), 603, 459, 441, 413, 395.

β-D-Glucopyranosyl 3β-(β-D-Glucopyranosyloxy)lup-20(29)-en-28-oate **(11a)**

Deacetylation of glucoside acetate **10a** (20 mg, 0.02 mmol) afforded glucoside **11a** (9 mg, 64%), m.p. 211–212 °C (methanol), $[\alpha]_D$ –5° (*c* 0.42, methanol). Reported[25] m.p. 209–211 °C, $[\alpha]_D$ –5° (ethanol). FAB-MS, *m/z*: 803 (M + Na), 619, 601, 439.

28-(β-D-Glucopyranosyloxy)lup-20(29)-en-3-one (**17a**)

Deacetylation of glucoside acetate **16a** (30 mg, 0.04 mmol) afforded glucoside **17a** (16 mg, 53%), m.p. 202–206 °C (methanol), $[\alpha]_D$ +2° (*c* 0.29, methanol). FAB-MS, *m/z*: 625 (M + Na), 603 (M + H), 441, 423.

28-(β-D-Glucopyranosyloxy)lupan-3-one (**17b**)

Deacetylation of glucoside acetate **16b** (30 mg, 0.04 mmol) afforded glucoside **17b** (20 mg, 85%), m.p. 210–211 °C (methanol), $[\alpha]_D$ –15° (*c* 0.51, methanol). FAB-MS, *m/z*: 627 (M + Na), 605 (M + H), 443, 425.

28-(β-D-Glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-diene-3-nitrile (**21a**)

Deacetylation of glucoside acetate **20a** (165 mg, 0.20 mmol) afforded glucoside **21a** (117 mg, 91%), m.p. 147–149/218–225 °C (methanol), $[\alpha]_D$ +4° (*c* 0.55, methanol). FAB-MS, *m/z*: 600 (M + H), 438, 420.

28-(β-D-Glucopyranosyloxy)-3,4-secolup-4(23)-ene-3-nitrile (**21b**)

Deacetylation of glucoside acetate **20b** (12 mg, 0.01 mmol) afforded glucoside **21b** (8 mg, 85%), m.p. 130–133 °C (methanol), $[\alpha]_D$ –16° (*c* 0.35, methanol). FAB-MS, *m/z*: 602 (M + H), 440, 422.

Methyl 28-(β-D-Glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-dien-3-oate (**28a**)

Deacetylation of glucoside acetate **27a** (158 mg, 0.20 mmol) afforded glucoside **28a** (86 mg, 69%), m.p. 149–151 °C (methanol), $[\alpha]_D$ 0° (*c* 0.50, methanol). FAB-MS, *m/z*: 655 (M + Na), 633 (M + H), 471, 453.

Methyl 28-(β-D-Glucopyranosyloxy)-3,4-secolup-4(23)-en-3-oate (**28b**)

Deacetylation of glucoside acetate **27b** (170 mg, 0.21 mmol) afforded glucoside **28b** (125 mg, 93%), m.p. 135–138 °C (methanol), $[\alpha]_D$ –23° (*c* 0.64, methanol). FAB-MS, *m/z*: 657 (M + Na), 473, 455.

28-(β-D-Glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-dien-3-oic Acid (**29a**)

Glucoside **28a** (96 mg, 0.15 mmol) was dissolved in a 3% solution of sodium hydroxide (6 mmol) in methanol (8 ml) and the solution was set aside at room temperature for 2 days. The reaction mixture was acidified with 20% acetic acid and the solvents were evaporated at 30 °C under diminished pressure. The residue was extracted with a chloroform–methanol mixture (5 : 1) and the extract was filtered through a layer of silica gel. Yield 86 mg (91%) of glucoside **29a**, m.p. 287–290 °C (chloroform–ethanol), $[\alpha]_D$ +3° (*c* 0.55, methanol). FAB-MS, *m/z*: 641 (M + Na), 619 (M + H), 457, 439.

28-(β-D-Glucopyranosyloxy)-3,4-secolup-4(23)-en-3-oic Acid (**29b**)

Using the same procedure as described for the preparation of glucoside **29a**, glucoside **28b** (70 mg, 0.11 mmol) was converted into amorphous glucoside **29b** (60 mg, 88%), $[\alpha]_D$ –16° (*c* 0.51, methanol). FAB-MS, *m/z*: 643 (M + Na), 459, 441.

3,28-Bis(β-D-glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-diene (**37a**)

Deacetylation of glucoside acetate **36a** (180 mg, 0.16 mmol) afforded amorphous glucoside **37a** (95 mg, 76%), $[\alpha]_D$ 0° (*c* 0.48, methanol).

3-(β-D-Glucopyranosyloxy)-3,4-secolupa-4(23),20(29)-dien-28-ol (**39a**)

Deacetylation of glucoside acetate **38a** (27 mg, 0.03 mmol) afforded amorphous glucoside **39a** (14 mg, 66%), $[\alpha]_D$ +19° (*c* 0.48, methanol). FAB-MS, *m/z*: 627 (M + Na), 605 (M + H), 437, 425.

Dimethyl 28-(β-D-Glucopyranosyloxy)-2,3-secolup-20(29)-ene-2,3-dioate (**47a**)

Deacetylation of glucoside acetate **46a** (70 mg, 0.08 mmol) afforded amorphous glucoside **47a** (50 mg, 89%), $[\alpha]_D$ –2° (*c* 0.49, methanol). FAB-MS, *m/z*: 701 (M + Na), 679 (M + H), 619, 517, 499, 457, 439.

Dimethyl 28-(β-D-Glucopyranosyloxy)-2,3-secolupane-2,3-dioate (**47b**)

Deacetylation of glucoside acetate **46b** (120 mg, 0.14 mmol) afforded amorphous glucoside **47b** (70 mg, 73%), $[\alpha]_D$ –22° (*c* 0.44, methanol). FAB-MS, *m/z*: 703 (M + Na), 681 (M + H), 621, 519, 501, 459, 441.

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