Carbohydrate Research, 207 (1990) 39–56
Elsevier Science Publishers B.V., Amsterdam

Synthesis and n.m.r. spectral properties of grape monoterpenyl glycosides

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(Received March 30th, 1989; accepted for publication in revised form, January 20th, 1990)

ABSTRACT

Several grape 6-*O*-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranosides and 6-*O*-α-L-arabinofuranosyl-β-D-glucopyranosides having (*E*)- and (*Z*)-3,7-dimethyl-2,6-octadien-1-yl, (*R,S*)-3,7-dimethyl-1,6-octadien-3-yl, (*R,S*)-1-methyl-1-(4-methyl-3-cyclohexen-1-yl)ethyl, benzyl, and 2-phenylethyl as aglycon group, as well as such diglycosides of chromogenic 4-nitrophenol, were synthesized by two methods, one involving mercuric cyanide-catalyzed glycosylation with glycosyl halides, and the other by acid-catalyzed glycosylation with glycosyl trichloracetimidates. Their ^{1}H- and ^{13}C-n.m.r. spectra, especially the glycosylation shifts of the ^{13}C-signals, were investigated.

INTRODUCTION

Since Cordonnier and Bayonove[1] first suggested that the fruit of *Vitis vinifera* var. Muscat of Alexandria contained monoterpene glycosides, extensive research has been carried out on their structural, chemical, and biochemical properties[2]. Indeed, they make up a stock for aroma which may be more abundant than the free odoriferous components[3].

Williams *et al.*[4,5] first identified them as 6-*O*-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranosides (β-rutinosides) and 6-*O*-α-L-arabinofuranosyl-β-D-glucopyranosides with monoterpenyl aglycons at the linalool oxidation state, and benzyl and 2-phenylethyl aglycons. Subsequent work has shown that other volatile flagrant compounds (or their precursors) are also present as disaccharide glycosides[6–10]. We report herein the chemical synthesis and the ^{1}H- and ^{13}C-n.m.r. caracteristics of these glycosides, as well as such diglycosides of 4-nitrophenol required as chromatographic standards and as models for enzymic studies[11].

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0008-6215/90/$03.50

RESULTS AND DISCUSSION

In a previous note[12], we have shown that the method described earlier by Bourbouze[13] for the synthesis of 4-nitrophenyl β-rutinoside hexaacetate (**17**) from 2,3,4,2′,3′,4′-hexa-*O*-acetyl-α-rutinosyl chloride (**3**) and 4-nitrophenol could not be used to prepare (*E*)-3,7-dimethyl-2,6-octadienyl β-rutinoside hexaacetate (**11**) (geranyl β-rutinoside hexaacetate). The latter compound was stereoselectively synthesized by condensation of 2,3,4-2′,3′,4′-hexa-*O*-acetyl-α-rutinosyl bromide (**4**) with geraniol in the presence of the Helferich catalyst [mercury(II) cyanide] in acetonitrile. These conditions gave a low but better yield than those already reported[4]; they were also used by us to synthesize (*R,S*)-1-methyl-1-(4-methyl-3-cyclohexen-1-yl)-ethyl β-rutinoside hexaacetate (**14**), as well as some monoterpenyl β-D-glucoside tetraacetates from commercial 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide[14].

However, the sensitive, less-reactive tertiary allylic alcohol, 3,7-dimethyl-1,6-octadien-3-ol (linalool), gave very poor yield when treated with **4** under the same conditions. Another main drawback of this glycosidation method is the low thermal stability and the highly sensitivity to hydrolysis of the starting diglycosyl halide[15] **4**, generated in mixture with the 1-*O*-deacetylated product **5** under relatively harsh conditions from commercial β-rutinose heptaacetate (**1**); rather than purify **4**, it was preferable to use it as a crude product in the glycosidation step, owing to the easy separation by column chromatography of the monoterpenyl β-rutinoside hexaacetates from the hydrolysis product **5**.

The starting material **2** for the synthesis of **32–38** is not readily available. The most efficient synthesis[16] requires several steps from D-glucose and L-arabinose, the key step being the triphenylmethylium perchlorate-catalyzed, stereocontrolled glycosylation of 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose by 3,5-di-*O*-acetyl-1,2-*O*-[(1-*exo*- and 1-*endo*-cyano)ethylidene]-β-L-arabinofuranose. Therefore, we developed a more efficient glycosylation[17] by the stereoselective anomeric activation of the *O*-acetyl derivatives **1** and **2** through formation of the stable *O*-glycosyl trichloracetimidates **9** and **10**. These compounds are readily available from unsubstituted **5–8** by base catalysis[18] of OAc-1 of **1** and **2** using either benzylamine in chloroform[18] for **1** or ammonia in methanol–oxolan[19] for **2**. The ratios of α to β anomers in **5, 6** and **7, 8** are about the same, as determined by ^{1}H-n.m.r. (4:1 and 3:1, respectively). Owing to the reversibility of *O*-glycosyl imidate formation, the thermodynamically more stable 1-*O*-α-(trichloracetimidates) **9** and **10** were obtained highly diastereoselectively and were substantially pure, as shown by ^{1}H- and ^{13}C-n.m.r. spectrometry.

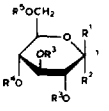
Glycosylation of the monoterpenols [geraniol, (*Z*)-3,7-dimethyl-2,6-octadienol (nerol), (±)-linalool, and (±)-α-terpineol], of the aromatic alcohols (benzyl and 2-phenylethyl alcohol), and of 4-nitrophenol with the trichloroacetimidates **9** and **10** was carried out with a slight excess of the nucleophiles under acid catalysis (boron trifluoride etherate) at room temperature in dichloromethane as solvent. With the monoterpenols, known to rearrange under acid conditions, glycosylated products of rearrangment were hardly observed. The glycosylation proceeded highly stereoselectively through the

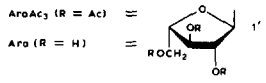
formation of a transient α-acyloxonium ion by C-2 acetyloxy participation[17,18], giving in fairly good yield the acetylated β-D-glycosides **11–24**. Compounds **11–24** were efficiently deacetylated in methanol under base catalysis, as previously reported[12,14] for **11** and **14**, to give the expected β-diglycosides **25–38**.

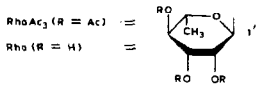
Another approach to the synthesis of the diglycosides **18–24** was to glycosylate the readily available 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucosides of the above mentioned alcohols (monoterpenols and aromatic alcohols) and 4-nitrophenol with 3,5-di-*O*-acetyl-1,2-*O*-[(1-*exo*- and 1-*endo*-cyano)ethylidene]-β-L-arabinofuranose according to the method of Backinowsky *et al.*[16]. However, this reaction gave no detectable diglycosides with the alcohol derivatives, probably owing to the attack by the triphenyl carbocation of the terpenyloxy residue, leading to a stable allylic terpenyl carbocation. Furthermore, the reaction proceeded with partial migration of the acetyl group from O-4 to O-6 of the sugar residue in the case of 4-nitrophenol, yielding a mixture of the (1→6) and (1→4)-linked diglycosides **24** and **39**. Such migration has been reported during detritylation of 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-β-D-galactopyranose[20].

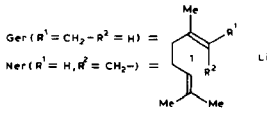
N.m.r. study. — The structures of the per-*O*-acetylated and unprotected diglycosides obtained were established by ^{1}H- and ^{13}C-n.m.r. spectromety (Tables I, II, and III). The ^{1}H- and ^{13}C-n.m.r. spectra were interpreted with the aid of homonuclear ^{1}H–^{1}H and selective heteronuclear ^{1}H–^{13}C double-resonance spectrometry and by reference to data for the diglycosides, [4,12,16,21] **1–3, 11,12, 17–20** for related compounds[18,19,22–29] and for monoterpenes[30,31] previously reported. In addition, the signals for the diastereoisomer mixtures [diglycosides of (*R,S*)-linalool and (*R,S*)-α-terpineol] were assigned by use of the data obtained for the β-D-glucoside of (*S*)-linalool and (*R*)-α-terpineol, which will be reported elsewhere[32]; these assignments were facilitated for **14, 21, 28** and **35** as the relative concentrations of the two diastereoisomers were significantly different (1:2). All chemical shifts and coupling constants reported in Tables I–III are in good agreement with those of the literature.

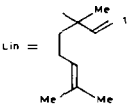
Chemical shifts of sugar units. — When examined separately, the acetylated diglycosides **11–24** and the unprotected diglycosides **25–38** (Tables I–III), showed all the signals for the D-glucopyranosyl residue protons and carbon atoms at almost the same position with about the same ^3J coupling constants between the protons, except for those of H-1, C-1, and C-2. A similar observation was made for all the signals for the protons and carbon atoms of the nonreducing sugar groups L-rhamnopyranosyl and L-arabinofuranosyl, in the related diglycosides. These ^{1}H- and ^{13}C-n.m.r. data suggest that the sugar units, β-D-glucopyranose, α-L-rhamnopyranose, and α-L-arabinofuranose, have similar conformational equilibrium with the same orientation of the interglycosidic bonds in related diglycosides, regardless of the structure of the aglycon. This indicated a preponderance of the $^4C_1$ (D) conformation for the D-glucopyranosyl residue with a 1,2-*trans*-diequatorial configuration of the glycosyl bond ($J_{1,2} \sim 8$ Hz, $J_{2,3} = \sim J_{3,4} = \sim J_{4,5} = \sim 9$ Hz), a preponderance of the $^1C_4$ (L) conformation for the L-rhamnopyranosyl group with a 1,2-*trans*-diaxial configuration of the glycosyl bond ($J_{1',2'} < 1.5$ Hz, $J_{2',3'} \sim 3.5$ Hz, $J_{3',4'} = \sim J_{4',5'} = \sim 9.5$ Hz), and a preponderance of a conformation close to E_0 with a 1,2-*trans*-quasi-anti configuration of the L-arabinofura-

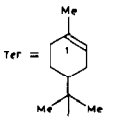


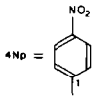












1 R^1=OAc, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
2 R^1=OAc, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
3 R^1=H, R^2=Cl, R^3=R^4=Ac, R^5=$RhaAc_3$
4 R^1=H, R^2=Br, R^3=R^4=Ac, R^5=$RhaAc_3$
5 R^1=H, R^2=OH, R^3=R^4=Ac, R^5=$RhaAc_3$
6 R^1=OH, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
7 R^1=H, R^2=OH, R^3=R^4=Ac, R^5=$AraAc_3$
8 R^1=OH, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
9 R^1=H, R^2=$Cl_3CC(=NH)O$–, R^3=R^4=Ac, R^5=$RhaAc_3$
10 R^1=H, R^2=$Cl_3CC(=NH)O$–, R^3=R^4=Ac, R^5=$AraAc_3$
11 R^1=GerO, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
12 R^1=NerO, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
13 R^1=LinO, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
14 R^1=TerO, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
15 R^1=BzlO, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
16 R^1=$PhCH_2CH_2O$, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
17 R^1=4NpO, R^2=H, R^3=R^4=Ac, R^5=$RhaAc_3$
18 R^1=GerO, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
19 R^1=NerO, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
20 R^1=LinO, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
21 R^1=TerO, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
22 R^1=BzlO, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
23 R^1=$PhCH_2CH_2O$, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
24 R^1=4NpO, R^2=H, R^3=R^4=Ac, R^5=$AraAc_3$
25 R^1=GerO, R^2=R^3=R^4=H, R^5=Rha
26 R^1=NerO, R^2=R^3=R^4=H, R^5=Rha
27 R^1=LinO, R^2=R^3=R^4=H, R^5=Rha
28 R^1=TerO, R^2=R^3=R^4=H, R^5=Rha
29 R^1=BzlO, R^2=R^3=R^4=H, R^5=Rha
30 R^1=$PhCH_2CH_2O$, R^2=R^3=R^4=H, R^5Rha
31 R^1=4NpO, R^2=R^3=R^4=H, R^5=Rha
32 R^1=GerO, R^2=R^3=R^4=H, R^5=Ara
33 R^1=NerO, R^2=R^3=R^4=H, R^5=Ara
34 R^1=LinO, R^2=R^3=R^4=H, R^5=Ara
35 R^1=TerO, R^2=R^3=R^4=H, R^5=Ara
36 R^1=BzlO, R^2=R^3=R^4=H, R^5=Ara
37 R^1=$PhCH_2CH_2O$, R^2=R^3=R^4=H, R^5=Ara
38 R^1=4NpO, R^2=R^3=R^4=H, R^5=Ara
39 R^1=4NpO, R^2=H, R^3=R^5=Ac, R^4=$AraAc_3$
40 R^1=R^3=R^4=H, R^2=OH, R^5=Rha
41 R^1=OH, R^2=R^3=R^4=H, R^5=Rha
42 R^1=R^3=R^4=H, R^2=OH, R^2=Ara
43 R^1=OH, R^2=R^3=R^4=H, R^5=Ara
44 R^1=4NpO, R^2=H, R^3=R^4=Ac, R^5=CPh_3

TABLE I

^{1}H-N.m.r. chemical shifts (δ) for the acetylated (**5–8, 12–24**) and the unprotected (**26–38**) disaccharide derivatives[a]

Compd.	*D-Glucose residue*							*Nonreducing glycosyl group*							*Glycosidic acetates*	*Aglycon residue*										
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6b*	*H-1'*	*H-2'*	*H-3'*	*H-4'*	*H-5'a*	*H-5'b*	*H-6'*		*H-1*	*H-1'*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*	*H-9*	*H-10*	*Ph*
5	5.41	4.85	5.54	4.88	4.29	3.57	3.74	4.84	5.31	5.25	5.05	3.89		1.20	1.98–2.14												
6	4.80					3.61	3.76																				
7	5.40	4.85	5.54	4.93	4.31[b]	3.64	3.73	5.16	5.06	4.98	4.31[b]	4.22	4.39		2.00–2.15												
8	4.77				4.01	3.65	3.79																				
12	4.53	4.95	5.20	4.98	3.68[b]	3.68[b]	3.68[b]	4.79	5.26[b]	5.26[b]	5.06	3.87		1.21	1.98–2.13	4.14	4.24	5.26[b]		2.03[b]	2.03[b]	5.08[b]		1.60	1.68	1.75	
13(*R*)	4.55	4.94[b]	5.21[b]	4.94[b]	3.63[b]	3.63[b]	3.63[b]	4.78[c]	5.21[b]	5.21[b]	5.05	3.84		1.21	1.98–2.13	5.21[b]	5.21[b]	5.89		1.60[b]	2.00[b]	5.05[b]		1.61	1.65	1.25	
13(*S*)	4.58	4.94	5.21	4.94	3.63	3.63	3.63	4.79[c]	5.21	5.21	5.05	3.84		1.21	1.98–2.13	5.21	5.21	5.71		1.60	2.00	5.05		1.61	1.65	1.31	
14(*R*)	4.69	4.94	5.22[b]	4.93	3.67[b]	3.59	3.67[b]	4.79	5.22[b]	5.22[b]	5.04	3.85		1.21	1.97–2.13			5.33	1.90[b]	1.55[b]	1.20[b]	1.90[b]	1.62		1.18	1.19	
14(*S*)	4.69	4.94	5.22	4.93	3.67	3.59	3.67	4.79	5.22	5.22	5.04	3.85		1.21	1.97–2.13			5.33	1.90	1.55	1.20	1.90	1.62		1.13	1.17	
15	4.48	4.96	5.11	4.89	3.62[b]	3.62[b]	3.62[b]	4.78	5.22[b]	5.22[b]	5.00	3.82		1.15	1.92–2.04	4.80	4.55										7.24[b]
16	4.45	4.93	5.15	4.91	3.65[b]	3.65[b]	3.65[b]	4.79	5.23	5.24	5.03	3.84[b]		1.19	1.86–2.08	4.09	3.65	2.86									7.25[b]
18	4.52	4.95	5.19	5.02	3.64[b]	3.64[b]	3.78[b]	5.08	5.07	4.98	4.29	4.23[b]	4.41		2.00–2.14	4.23[b]	4.23[b]	5.26[b]		2.07[b]	2.07[b]	5.06[b]		1.62	1.70	1.66	
19	4.52	4.93	5.19	5.04	3.64[b]	3.64[b]	3.79[b]	5.07	5.07	4.99	4.29	4.22	4.40		2.00–2.14	4.15	4.23	5.27[b]		2.07[b]	2.07[b]	5.07[b]		1.62	1.70	1.77	
20(*R*)	4.50	4.92[b]	5.15[c]	4.92[b]	3.56[b]	3.56[b]	3.70[b]	5.03	5.05	4.92[b]	5.26[d]	4.19[e]	3.37[f]		1.96–2.14	5.11	5.12	5.88		1.51[b]	1.95[b]	5.01[b]		1.54[g]	1.63	1.21	
20(*S*)	4.54	4.92	5.14[c]	4.92	3.56	3.56	3.70	5.03	5.05	4.92	5.24[d]	4.18[e]	3.38[f]		1.96–2.14	5.21	5.15	5.69		1.51	1.95	5.01		1.55[g]	1.63	1.28	
21(*R*)	4.67	4.91	5.20	5.00	3.64[b]	3.59[b]	3.74[b]	5.06[h]	5.06[b]	4.96	4.28	4.21	4.40		1.99–2.13			5.34	1.90[b]	1.55[b]	1.18[b]	1.90[b]	1.63		1.14	1.16	
21(*S*)	4.67	4.92	5.20	5.01	3.64	3.59	3.74	5.06	5.06	4.96	4.28	4.21	4.40		1.99–2.13			5.34	1.90	1.55	1.18	1.90	1.63		1.12	1.17	
22	4.55	5.02	5.17	5.04	3.68[b]	3.68[b]	3.79[b]	5.11	5.10	4.99	4.30	4.22	4.41		1.99–2.12	4.87	4.62										7.32[b]
23	4.47	4.94	5.16	5.01	3.66[b]	3.66[b]	3.77	5.08	5.07	4.97	4.28	4.21	4.40		1.89–2.10	4.09	3.66	2.87									7.23[b]
24	5.19	5.27	5.32	5.12	3.91	3.66	3.81	5.01	5.09	4.98	4.23	4.18	4.36		2.05–2.14			7.10	8.23		8.23	7.10					
26	4.11	2.95	3.12	3.00	3.21	3.43[b]	3.81	4.59	3.62	3.43[b]	3.17[b]	3.43[b]		1.13	–	4.05	4.15	5.29		2.03[b]	2.03[b]	5.08[b]		1.57	1.64	1.71	
27(*R*)	4.15	2.94[b]	3.12[b]	2.94[b]	3.12[b]	3.39[b]	3.77	4.57	3.59	3.39[b]	3.17[b]	3.39[b]		1.12	–	5.10	5.15	5.95		1.50[b]	1.96[b]	5.08[b]		1.55	1.63	1.23	
27(*S*)	4.15	2.94	3.12	2.94	3.12	3.39[b]	3.77	4.57	3.59	3.39	3.17	3.39		1.12	–	5.14	5.20	5.86		1.50	1.96	5.08		1.55	1.63	1.26	
28(*R*)	4.27	2.89	2.99	2.97	3.16	3.37[b]	3.77	4.53	3.58[b]	3.37[b]	3.14	3.37[b]		1.09	–			5.29	1.90[b]	1.60[b]	1.11[b]	1.90[b]	1.55		1.05	1.08	
28(*S*)	4.27	2.89	2.99	2.97	3.16	3.37	3.77	4.54	3.58	3.37	3.14	3.37		1.09	–			5.29	1.90	1.60	1.11	1.90	1.55		1.05	1.08	
29	4.19	3.01	3.13	3.02	3.25	3.47	3.81	4.62	3.64	3.47	3.18	3.47		1.17	–	4.73	4.53										7.33[b]
30	4.18	2.90	3.14	3.00	3.27	3.44[b]	3.80	4.59	3.61	3.44[b]	3.17	3.44[b]		1.13	–	3.88	3.67	2.84									7.23[b]
31	5.09	3.36[b]	3.36[b]	3.22[b]	3.70[b]	3.49[b]	3.89	4.58	3.70[b]	3.49[b]	3.22[b]	3.49[b]		1.15	–			7.25	8.26		8.26	7.25					
32	4.13	2.95	3.13	3.00	3.25	3.41	3.86	4.80	3.79	3.62	3.72	3.42	3.54		–	4.09	4.19	5.26		2.01[b]	2.01[b]	5.08[b]		1.54	1.62	1.59	
33	4.13	2.94	3.13	3.00	3.26	3.40	3.86	4.79	3.80	3.63	3.73	3.42	3.56		–	4.05	4.18	5.25		2.03[b]	2.03[b]	5.09[b]		1.57	1.65	1.71	
34(*R*)	4.15	2.92[b]	3.10	2.97[d]	3.12	3.41	3.78	4.76[e]	3.76	3.62[f]	3.72	3.34	3.53		–	5.08	5.11	5.93		1.49[b]	1.93[b]	5.05[b]		1.52	1.61	1.21	
34(*S*)	4.15	2.93[c]	3.10	2.98[d]	3.12	3.41	3.78	4.75[e]	3.76	3.63[f]	3.72	3.34	3.53		–	5.13	5.17	5.83		1.49	1.93	5.05		1.52	1.61	1.24	
35(*R*)	4.29	2.89	3.15	2.99[c]	3.23	3.41[d]	3.81	4.74[e]	3.77[f]	3.61[g]	3.71[h]	3.34[i]	3.53		–			5.31	1.91[b]	1.61[b]	1.09[b]	1.91[b]	1.60		1.07	1.10	
35(*S*)	4.29	2.89	3.15	2.98[c]	3.23	3.40[d]	3.81	4.76[e]	3.76[f]	3.60[g]	3.72[h]	3.35[i]	3.53		–			5.31	1.91	1.61	1.09	1.91	1.60		1.07	1.10	
36	4.24	3.03	3.13	3.03	3.30	3.44	3.90	4.84	3.84	3.64	3.75	3.41	3.56		–	4.79	4.58										7.34[b]
37	4.21	2.96	3.15	2.99	3.30	3.40	3.87	4.79	3.80	3.62	3.73	3.41	3.55		–	3.91	3.68	2.86									7.23[b]
38[j]	5.15	3.52[b]	3.52[b]	3.44	3.74	3.55	3.98[b]	4.91	3.98[b]	3.81	3.93	3.62	3.66		–			7.11	8.11		8.11	7.11					

[a] Acetylated compounds in $CDCl_3$ and unprotected compounds in $(CD_3)_2SO$ (internal standard, Me_4Si). [b] Centre of a multiplet. [c–i] Assignments may be interchanged in each numbered compound. [j] Recorded in D_2O.

TABLE II

^{1}H-N.m.r. first-order coupling constants (Hz) for the acetylated (**5–8, 12–24**) and unprotected (**26–38**) disaccharide derivatives[a]

Compd.[b]	D-*Glucose residue*							L-*Arabinose residue*						L-*Rhamnose residue*					*Aglycon residue*				
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'a}$	$J_{4',5'b}$	$J_{5'a,5'b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{5,6}$
5	3.7	10.0	9.5	10.3	7.3	1.9	11.9							1.9	3.5	10.0	9.7	6.3					
6	7.9					2.0	12.0																
7	3.6	10.2	9.7	9.6	6.9	2.1	12.2	<1	1.8	5.2	5.7	3.4	11.5										
8	8.0				6.2	2.0	11.3																
12	7.9	9.7	9.2	9.2										~1	3.3	9.7	9.8	6.3	11.7	7.8	6.6		
13[b]	8.0													~1			9.7	6.3	~1.5	11.1	17.6		
14[b]	8.0	9.7	9.4	9.4	7.4		11.8							1.5		9.7	9.7	6.3					
15	8.0	9.6	9.5	9.5										1.5		9.9	9.8	6.3	12.4				
16	7.9	9.7	9.5	9.4										~1	3.5	9.6	9.7	6.3	9.6	6.1	6.1		
18	7.9	9.5	9.4	9.5				<1	1.5	5.4	5.6	3.2	11.5										
19	8.0	9.4	9.4	9.4				<1	1.3	5.3	5.4	3.2	11.6						11.5	7.8	5.4		
20[b]	8.0	9.5	9.5					<1	1.7	5.4	5.4	3.3	11.6						1.8	11.0	17.7		
21[b]	8.0	9.6	9.5	9.5	5.9		10.7	<1	1.4	5.2	5.4	3.1	11.5										
22	8.0	9.4	9.4	9.4				<1	1.6	5.1	5.7	3.4	11.7						12.3				
23	7.9	9.6	9.6	9.5		<1	9.5	<1	1.5	5.4	5.6	3.2	11.5						9.6	6.3	6.3		
24	7.3	9.2	8.7	9.7	6.5	2.2	11.6	<1	1.6	5.2	5.5	3.1	11.4									9.0	9.0
26	7.8	8.9	8.8	9.3	6.7	1.5	11.3							1.2	3.0	9.6	9.6	6.2	12.0	7.8	6.6		
27[b]	7.7					1.0	11.2							1.5		9.2	9.2	5.9	1.2	10.9	17.9		
28[b]	7.7	9.0	9.0	9.0		1.0	11.3							1.3	3.4	8.9	8.9	6.2					
29	7.8	8.8	8.8	9.3	5.6	<1	11.0							~1	3.3	9.3	9.3	6.2	12.1				
30	7.8	9.0	9.2	9.3	6.9	1.4	11.3							1.3	3.0	9.4	9.4	6.2	9.9	7.2	7.4		
31	7.5					1.2	11.0							1.3		9.3	9.3	6.2				9.3	9.3
32	7.8	9.0	9.0	9.3	6.5	1.5	11.1	1.8	3.9	6.6	5.8	3.0	11.4						12.0	7.8	6.6		
33	7.8	9.0	9.0	9.5	6.9	1.5	11.1	1.8	4.0	6.8	5.5	3.2	11.5						12.0	7.5	6.5		
34[b]	7.7	9.0	8.9	9.6	5.6	1.0	11.8	1.6	4.2	6.3	6.0	3.2	11.8						1.4	11.0	17.7		
35[b]	7.7	9.0	9.0	9.2	5.5	1.4	11.6	1.7	3.9	6.8	5.4	3.2	11.8										
36	7.7	9.0	9.0	9.6	7.3	1.7	11.2	1.9	4.0	6.8	5.8	3.3	12.0						12.2				
37	7.8	8.8	8.8	9.4	5.8	1.5	11.4	1.8	4.2	6.7	5.7	3.2	11.7						9.7	7.2	7.2		
38	7.1		9.3	9.3	5.7	1.0	11.3	~1	3.1	5.8	5.8	3.4	11.5									9.2	9.2

[a] See footnote *a* to Table I. [b] The coupling constants for each diastereoisomer are approximatively equal.

nosyl bond for the L-arabinofuranosyl group when acetylated[16,33] ($J_{1',2'} < 1$ Hz, $J_{2',3'} \sim 1.5$ Hz, $J_{3',4'} \sim 5.2$ Hz), and a slight deformation for the nonacetylated compound ($J_{1',2'}$ and $J_{2',3'}$ are slightly increased). In contrast, the signal for H-1 of the D-glucopyranosyl group was displaced slightly upfield (0–0.3 p.p.m.) (when compared to that for the corresponding free β anomer of the disaccharides **6** and **8**) on glycosylation with monoterpenols and arylalkyl alcohols, whereas glycosylation with 4-nitrophenol resulted in a downfield shift, not only of the signal for H-1 but also of those for H-2,3,4,5.

On glycosylation with tertiary alcohols, such as linalool and α-terpineol, the signal for C-1 in **13, 14, 20, 21, 27, 28, 34,** and **35** remained almost constant comparatively to that for the corresponding free β anomer of the disaccharides **6, 8, 41,** and **43**. In contrast, it was deshielded on glycosylation with 4-nitrophenol in **17, 24, 31,** and **38**, and with the primary alcohols in **11, 12, 15, 16, 18, 19, 22, 23, 25, 26, 29, 30, 32, 33, 36,** and **37** (Table IV) in the increasing order, 4-nitrophenol, allylic and benzylic alcohols, and 2-phenylethanol. The C-2 signal was displaced slightly upfield on glycosylation with all the O-nucleophiles used (~ -2 p.p.m. for the acetylated glycosides **11–24** and ~ -1 p.p.m. for the unprotected glycosides **25–38**). All the C-1 and C-2 glycosylation shifts observed (Table IV) were consistent with those previously reported for β-D-glucosides of primary and tertiary alcohols[34,39], and of phenols[40,42], although the data for the geranyl and neryl β-D-diglycosides **11, 12, 18, 19, 25, 26, 32,** and **33** were slightly decreased comparatively to the benzyl and 2-phenylethyl β-D-diglycosides **15, 16, 22, 23, 29, 30, 36,** and **37**, or to reported values for the β-D-glucosides of other primary alcohols[34–39].

Chemical shifts of aglycon residue. — The glycosylation shifts of the carbon signals of the aglycon residues are summarized in Table IV. As previously reported[34–39], the only significant glycosylation shifts are those for the C-1″ and C-2″ aglycon carbon atoms, but the C-3″ aglycon carbon atom displayed a significant glycosylation downfield shift when it is sp2 hybridized (geraniol, nerol, linalool, and benzyl alcohol). The glycosylation shifts observed between the two sets of diglycosides, β-rutinosides (**11–17**, and **25–31**) and 6-*O*-α-L-arabinofuranosyl-β-D-glucopyranosides (**18–24** and **32–38**) were very similar for comparable compounds, *i.e.*, same aglycon and same protecting group.

Moreover, the values observed between the two sets of acetylated (**11–24**) and unprotected (**25–38**) diglycosides for a given aglycon group showed the same trends but are slightly different, as previously reported for β-D-glucosidation[37]; it should be noted, as indicated in Table IV, that the ^{13}C-n.m.r. spectra of the unprotected glycosides were recorded for compounds in D_2O solution and compared to the ^{13}C-n.m.r. spectra of aglycon groups recorded for compounds in $CDCl_3$ solution. Table IV shows also significant differences for the glycosylation shifts between the diglycosides of the two types of alcohols, primary and tertiary, when considering similar carbon atoms. Interestingly, the values observed for the former (primary alcohols) are quite similar to those observed generally for β-D-glucosides of primary, but also of unhindered secondary and tertiary alcohols[34–39,43], whereas those observed for the latter (linalool and α-terpineol) are quite similar to those observed for β-D-glucosides of hindered secondary

TABLE III

^{13}C-N.m.r. chemical shifts (δ) for the acetylated (**5–8, 12–24**) and unprotected (**25–38**) disaccharide derivatives[a]

Compd.	*D-Glucose residue*						*Nonreducing glycosyl group*						*Nonaromatic carbon atoms*										*Aromatic carbons atoms*			
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*C-1*	*C-2/6*	*C-3/5*	*C-4*
5α	89.9	69.1[b]	69.4[b]	69.2[b]	71.2[b]	67.8	98.4	70.0	69.9	70.9	66.9	17.4														
6β	95.4	72.5	73.0[b]	69.3[b]	73.9[b]	67.7	98.6	70.0	69.9	70.9	66.9	17.4														
7α	90.2	69.6[b]	70.3	69.3[b]	71.5	67.2	106.8	82.1	77.3	80.3	63.6															
8β	95.7	72.8	73.4[b]	69.6	73.9[b]	66.9	106.8	81.7	77.3	80.5	63.6															
12[i]	99.3	71.5	73.1[b]	69.0	73.1[b]	67.2	98.2	69.6[c]	69.7[c]	71.1	66.6	17.4	65.4	120.4	142.1	32.1	26.7	123.8	132.0	25.7	17.7	23.5				
13(*R*)	95.6	71.6	73.0[b]	69.1	73.2[b]	67.0	98.1[c]	69.5[d]	69.7[d]	71.1	66.6	17.4	115.2	142.0	80.7[e]	40.8	22.2[f]	124.1[g]	131.7	25.6	17.5[h]	22.4				
13(*S*)	96.1	71.6	73.0	69.1	73.2	67.0	98.2[c]	69.5	69.7	71.1	66.6	17.4	116.5	141.5	80.8[e]	41.9	22.3[f]	124.2[g]	131.7	25.6	17.6[h]	23.1				
14(*R*	95.1	71.7	73.0[b]	69.1	73.2[b]	66.8	98.1	69.5[d]	69.7[d]	71.0	66.6	17.4	133.8	120.7	26.6	43.9	23.5	31.0	23.3	80.5	23.5	23.8				
14(*S*)	95.2	71.7	73.0	69.1	73.2	66.9	98.1	69.5	69.7	71.0	66.6	17.4	134.8	120.4	26.6	44.1	23.6	31.0	23.3	80.6	22.1	24.8				
15	99.3	71.4	72.9[b]	69.0	73.5[b]	67.0	98.2	69.5[c]	69.7[c]	71.1	66.7	17.4	70.7										137.0	128.5	127.7	127.9
16	100.7	71.3	72.8[b]	69.0	73.4[b]	67.1	98.2	69.5[c]	69.6[c]	71.1	66.7	17.4	70.5	35.9									138.7	129.0	128.3	126.3
18[i]	98.7	71.7	73.4	69.5	73.4	66.3	106.2	81.5	77.4	80.6	63.4		65.2	119.6	142.3	39.7	26.5	124.0	132.0	25.7	17.7	16.4				
19[i]	99.4	71.7	73.3[b]	69.4	73.4[b]	66.3	106.2	81.5	77.3	80.5	63.4		65.4	120.7	142.1	32.3	26.8	123.9	132.3	25.7	17.7	23.5				
20(*R*)	95.8	71.7	73.0[b]	69.5	73.4[b]	66.3	106.0	81.4	77.4	80.5	63.4		114.8	142.6	80.7[e]	40.7	22.3[d]	124.3	131.8	25.6	17.7	22.7				
20(*S*)	96.2	71.7	73.0	69.5	73.4	66.3	106.0	81.4	77.4	80.5	63.4		116.1	142.0	80.8[e]	41.9	22.4[d]	124.3	131.8	25.6	17.7	23.3				
21(*R*)	95.4	71.9	73.0[b]	69.6	73.5[b]	66.3	106.0	81.3	77.4	80.7	63.4		134.0	120.8	26.8	44.1	23.7	31.1	23.3	80.4	23.3	24.0				
21(*S*)	95.4	71.9	73.0	69.6	73.5	66.3	106.0	81.3	77.4	80.7	63.4		134.3	120.6	26.8	44.2	23.7	31.1	23.3	80.5	22.3	25.0				
22	99.5	71.7	73.3[b]	69.4	73.6[b]	66.3	106.3	81.5	77.4	80.6	63.5		70.7										137.2	128.7	127.9	128.2
23	100.8	71.5	73.1[b]	69.4	73.5[b]	66.3	106.2	81.4	77.3	80.5	63.4		70.5	36.1									138.7	129.1	128.5	126.5
24[b]	98.5	71.3	72.7	68.8	74.1	66.0	106.2	81.4	77.3	80.7	63.2												161.5	117.0	126.0	143.7

^{13}C-N.m.r. chemical shifts (δ) for the acetylated (**5–8, 12–24**) and unprotected (**25–38**) disaccharide derivatives[a]

Compd.	D-Glucose residue						Nonreducing glycosyl group						Nonaromatic carbon atoms										Aromatic carbons atoms			
	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1	C-2/6	C-3/5	C-4
25	101.2[b]	73.8	75.5	70.3	76.7	67.2	101.1[b]	71.1[c]	70.9[c]	72.9	69.4	17.5	66.0	119.6	144.3	39.7	26.5	124.9	133.6	25.9	17.9	16.3				
26[b]	101.2	73.8	75.4	70.3	76.7	67.1	101.2	71.0[c]	70.8[c]	72.9	69.4	17.5	66.1	120.4	144.3	32.0	26.7	124.5	134.4	25.7	17.8	23.4				
27(*R*)	97.9	73.9[b]	75.2	70.4[c]	76.7	67.1[d]	101.0	71.0[c]	70.9[c]	72.9	69.3	17.5	116.3	142.6	82.1[f]	39.9	22.7	125.2	133.7	25.7	17.8	23.1				
27(*S*)	98.1	74.0[b]	75.2	70.6[c]	76.7	67.2[d]	101.0	71.0	70.9	72.9	69.3	17.5	117.0	142.4	82.2[f]	41.1	22.7	125.2	133.7	25.7	17.8	23.1				
28(*R*)	97.3	74.1	75.1	70.7	76.8	67.3	101.1	71.0[b]	70.9[b]	72.9	69.4	17.5	136.6	121.8	27.3	43.6	24.4	31.2	23.3	82.6	23.5	24.0				
28(*S*)	97.4	74.1	75.1	70.4	76.8	67.3	101.2	71.0[b]	70.9[b]	72.9	69.4	17.5	136.7	121.7	27.5	43.5	24.3	31.4	23.3	82.7	22.6	24.8				
29	102.2	73.9	75.5	70.4	76.5	67.5	101.3	71.0[b]	70.8[b]	72.8	69.4	17.5	72.5										137.4	129.5	129.5	129.2
30	103.1	73.8	75.5	70.5	76.5	67.7	101.4	71.0[b]	70.8[b]	72.8	69.4	17.4	71.7	36.1									139.5	129.8	129.5	127.3
31	99.9	73.5	75.8	70.2	76.2	66.8	100.9	71.0[b]	70.8[b]	72.7	69.4	17.2											162.3	117.2	126.8	143.3
32	101.1	73.8	75.6	70.4	76.6	67.5	108.8	81.8	77.3	84.6	61.9		66.3	119.5	144.6	39.6	26.4	124.9	134.0	25.7	17.8	16.3				
33	101.4	73.8	75.5	70.4	76.6	67.4	108.8	81.8	77.3	84.7	61.9		66.2	120.6	144.4	32.1	26.8	124.5	134.5	25.7	17.8	23.4				
34(*R*)	97.8	73.9[b]	75.2	70.6	76.6	67.6[c]	108.9[d]	81.8	77.4	84.7	61.9		116.5	142.5	82.2	39.8	23.0	125.2	134.2	25.6	17.7	23.0				
34(*S*)	98.0	74.0[b]	75.2	70.6	76.6	67.8[c]	108.8[d]	81.8	77.4	84.7	61.9		117.0	142.4	82.3	40.9	23.0	125.2	134.2	25.6	17.7	23.0				
35(*R*)	97.3	74.1	75.2	70.7	76.7	67.8	108.9	81.8	77.4	84.7	61.9		136.6	121.7	27.2	43.6	24.4	31.2	23.3	82.6	23.5	23.9				
35(*S*)	97.4	74.1	75.1	70.5	76.7	67.6	108.8	81.8	77.4	84.6	61.8		136.7	121.7	27.5	43.5	24.3	31.2	23.3	82.7	22.6	24.7				
36	102.2	73.9	75.6	70.5	76.5	67.5	108.9	81.8	77.4	84.7	62.0		72.4										137.4	129.5	129.5	129.2
37	103.1	73.8	75.5	70.5	76.5	67.6	108.9	81.8	77.4	84.7	62.0		71.7	36.0									139.4	129.8	129.5	127.3
38	100.4	73.7	76.2[b]	70.4	76.4[b]	67.5	109.1	82.0	77.6	85.0	62.2												162.7	117.6	127.1	143.6

[a] For solutions in $CDCl_3$ for **5–8** and **12–24**, and D_2O for **25–38** (internal standard, tetramethylsilane). Other signals: CH_3CO, 20.6–20.9; CH_3CO, 169.1–170.7. [b] [b]Assignments may be interchanged in each numbered compound. [f] Compare with data published for the natural compounds[4].

TABLE IV

^{13}C-N.m.r. glycosidation shifts of the diglycosides **11–38**[a]

Aglycon	*Compd.*	*Glycosyl C-1*	*Aglycon carbon atoms* ($\Delta\delta_a$)				
		($\Delta\delta_s$)	*C-α*	*C-β*			Csp_2-*γ*
				Most hindered	*Others*		
Geraniol	**11**	+ 3.4	+ 6.5	− 5.2			+ 5.3
	18	+ 3.0	+ 6.5	− 4.9			+ 5.1
	25	+ 4.4	+ 7.3 (+ 2.6)[c]	−4.9 (−5.6)			+ 7.1 (+ 4.6)
	32	+ 4.3	+ 7.6	− 5.0			+ 7.4
Nerol	**12**	+ 3.9	+ 6.7	− 4.7			+ 3.5
	19	+ 3.7	+ 6.7	− 4.4			+ 3.5
	26	+ 4.5	+ 7.4 (+ 2.3)	− 4.7 (− 5.4)			+ 5.7 (+ 3.5)
	33	+ 4.6	+ 7.5	− 4.7			+ 5.8
(*R*)-Linalool	**13**(*R*)	+ 0.2	+ 8.0	− 0.4	− 4.8	− 3.0	+ 3.9
	20(*R*)	+ 0.1	+ 8.0	− 0.5	− 4.5	− 2.4	+ 3.5
	27(*R*)	+ 1.2	+ 9.4 (+ 10.1)	− 1.3 (− 1.5)	− 4.1 (− 3.4)	− 2.4 (− 2.9)	+ 5.0 (+ 1.7)
	34(*R*)	+ 1.0	+ 9.5	− 1.4	− 4.2	− 2.5	+ 5.2
(*S*)-Linalool	**13**(*S*)	+ 0.7	+ 8.1	+ 0.7	− 4.1	− 3.5	+ 5.2
	20(*S*)	+ 0.5	+ 8.1	+ 0.7	− 3.9	− 3.0	+ 4.8
	27(*S*)	+ 1.4	+ 9.5 (+ 10.1)	− 0.1 (− 1.5)	− 4.1 (− 3.4)	− 2.6 (− 2.9)	+ 5.7 (+ 1.7)
	34(*S*)	+ 1.2	+ 9.6	− 0.3	− 4.2	− 2.6	+ 5.7
(*R*)-α-Terpineol	**14**(*R*)	− 0.3	+ 8.3	− 1.1	− 3.8	− 2.2	
	21(*R*)	− 0.3	+ 8.2	− 0.9	− 3.8	− 2.0	
	28(*R*)	+ 0.6	+ 10.4 (+ 12.5)	− 1.4 (−2.3)	− 4.0 (− 4.0)	− 2.0 (−2.7)	
	35(*R*)	+ 0.5	+ 10.4	− 1.4	− 3.8	− 2.1	
(*S*)-α-Terpineol	**14**(*S*)	− 0.2	+ 8.4	− 0.9	− 3.9	− 2.5	
	21(*S*)	− 0.3	+ 8.3	− 0.8	− 3.4	− 2.5	
	28(*S*)	+ 0.7	+ 10.5 (+ 12.5)	− 1.5 (− 2.3)	− 3.7 (− 4.0)	− 2.3 (− 2.7)	
	35(*S*)	+ 0.6	+ 10.5	− 1.5	− 3.4	− 2.5	

Benzyl alcohol	**15**	+ 3.9	+ 6.2	− 3.8	+ 1.4
	22	+ 3.8	+ 6.2	− 3.6	+ 1.6
	29	+ 5.5	+ 8.0 (+ 1.6)	− 3.4 (− 4.6)	+ 2.4 (+ 1.4)
	36	+ 5.4	+ 7.9	− 3.4	+ 2.4
2-Phenylethanol	**16**	+ 5.3	+ 7.5	− 3.1	
	23	+ 5.1	+ 7.5	− 2.9	
	30	+ 6.4	+ 8.7	− 2.9	
	37	+ 6.3	+ 8.7	− 3.0	
4-Nitrophenol	**17**	+ 2.6	− 4.4		
	24	+ 2.8	− 3.9		
	31	+ 3.7	− 3.1		
	38	+ 3.6	− 2.7		

[a] $\Delta\delta_S$ and $\Delta\delta_A$ in p.p.m.. The glycosydation shifts for glycosidic C-1 were calculated as $\Delta\delta_S = \delta$ (R diglycoside) − δ (H diglycoside) from the chemical shifts reported in Table III for **11–24** (in $CDCl_3$) and **25–38** (D_2O), and those for the corresponding β anomer of the 1-*O*-unsubstituted diglycosides **6** and **8** (δ 95.4 and 95.7 in $CDCl_3$, respectively), **41** (ref. 21), and **43** (δ 96.7 and 96.8 in D_2O, respectively). The glycosidation shifts for the carbon signals of the aglycon residues, were calculated as $\Delta\delta_A$ = δ (R diglycoside) − δ (aglycon, RH) from the chemical shifts reported in Table III for **11–24** (in $CDCl_3$) or **25–38** (in D_2O) and those for the corresponding aglycon[29] compound (in $CDCl_3$). [b] The corresponding acetylation shifts[29] are given in parentheses.

alcohols[34–39,43] and of hindered tertiary alcohols of the dammarane type[36,38,39]. The differences observed for the β-D-glucosides of the hindered secondary alcohols[45] was attributed to the change in orientation of the β-D-glucosyl linkage due to a modification of the $\varphi(1)$ torsion angle[44] with the possibility of a substantial change in the bond angle ζ (C-1–O-1, aglycon C-1″)[44] around its assumed value of 113°, although the $\varphi(1)$ torsion angle[44] was expected to be constant ($\sim +65°$) owing to the exoanomeric effect[45]. Such considerations could explain the "anomalous" glycosylation shifts observed for the β-D-diglycosides of (±)-linalool (**12, 20, 27,** and **32**) and (±)-α-terpineol (**14, 21, 28,** and **35**), the long isoprenoïd chain in the linalyl residue or the carbon ring in the α-terpinyl residue exerting a steric effect like a substituent at C-2″ in a secondary hindered alcohol.

The data obtained for these diastereoisomeric diglycosides, however, showed surprisingly only a slight difference in their glycosylation shifts upon combination of the chiralities of the asymetric C-1 (D-glucosyl) and C-1″ or C-2″ (aglycon), contrary to the β-D-glucosides of asymetric, hindered secondary alcohols[34–39,43,45]. Therefore, a significant change in the bond angle ζ (C-1–O-1, aglycon C-1″) but also in the torsion angle $\varphi(1)$ could occur in these compounds, in which the important steric hindrance could override the exoanomeric effect. On the contrary, this effect could cause, in the β-D-glycosides of the primary alcohols, an important energy bias in favor of conformations having a $\varphi(1)$ torsion angle constant ($\sim +65°$) (as suggested for β-D-glucosides of secondary alcohols[45]), but having the long isoprenoïd chain in a geometry approximatively *anti* to the glycosyl residue about the O-1–C-1″ bond [as suggested for the β-(1→6) linkage of two D-glucose units[46]]. It is interesting to note the similarity between these glycosylation shifts and the acetylation shifts observed on acetylation of the monoterpenols[30,31], which shows also the difference observed between the derivatives of primary and tertiary monoterpenols (Table IV).

EXPERIMENTAL

General methods. — Melting points were recorded with a Büchi SMP-20 apparatus and optical rotations were measured with a Perkin–Elmer 241 polarimeter at 20 ±1°. N.m.r. spectra were recorded with a Bruker 360 MHz spectrometer (360 MHz for ^{1}H-n.m.r. and 50.323 MHz or 20.115 MHz for ^{13}C-n.m.r. spectra). Column chromatography was performed on Silica Gel 60 (63–200 μm or 40–63 μm Merck) and t.l.c. on Kieselgel 60 (Merck) with detection by charring with 10% H_2SO_4 in ethanol. The following solvent systems were used: (*A*) 4:1 petroleum ether–diethyl ether, (*B*) 1:1 petroleum ether–diethyl ether, (*C*) 3:7 petroleum ether–diethyl ether, (*D*) 4:1 dichloromethane–diethyl ether, (*E*) 3:2 dichloromethane–diethyl ether, (*F*) 1:1 petroleum ether–ethyl acetate, (*G*) petroleum ether–ethyl acetate gradient, (*H*) 4:1 petroleum ether–acetone, (*I*) 7:3 petroleum ether–acetone, (*J*) 4:1 chloroform–methanol, and (*K*) 13:6:2 ethyl acetate–2-propanol–water. Solutions were concentrated *in vacuo* at 40°. Dichloromethane was dried with $CaCl_2$ and distilled from $CaCl_2$, then from CaH_2. Benzene was distilled from CaH_2. Boron trifluoride etherate was distilled before each glycosylation. K_2CO_3 was dried *in vacuo* during 3 h.

*Neryl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-deoxy-α-*L*-mannopyranosyl)-β-*D*-glucopyranoside [neryl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-rhamnopyranosyl)-β-*D*-glucopyranoside* (**12**). — (*a*) *From α-rutinosyl bromide* [4](**4**). Compound **12** was obtained from **4** (1 mmol) and nerol (5.8 mmol) according to Baumes *et al.*[12] in a 20% yield.

(*b*) *From β-rutinose heptaacetate* (**1**). A solution of **1** (Sarynthèse; 3.75 mmol) in cold (0°) oxolan (80 mL) was treated with a solution of ammonia in methanol (25 mL; prepared by bubbling NH_3 through methanol at 0° for 10 min). The mixture was stirred at 0° until the starting material disappeared. The solution was concentrated and the crude residue was subjected to column chromatography (63–200 μm, *E*) to give 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α- (**5**) and -β-D-glucopyranose (**6**), syrup (3.56 mmol, 95%; ratio 5 to 6 in $CDCl_3$, 4:1); R_F 0.46 (*E*).

To a solution of **5** and **6** (3.08 mmol) in anhydrous dichloromethane (10 mL) were added trichloroacetonitrile (1.7 mL, 16.9 mmol) and anhydrous K_2CO_3 (1.7 g, 17 mmol). The mixture was stirred for 48 h at room temperature, and then diluted with dichloromethane (10 mL) and washed with cold water (2 × 25 mL). The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography (63–200 μm, *C*) of the crude residue gave, after crystallization from diethyl ether, 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-glucopyranosyl trichloroacetimidate (**9**; 2.21 mmol, 72%), m.p. 167–168°, R_F 0.4 (*D*); ^{1}H-n.m.r. ($CDCl_3$): δ 1.18 (d, 3 H, $J_{5',6'}$ 6.2 Hz, H-6'), 1.94–2.11 (6 s, 18 H, 6 AcO), 3.58 (dd, 1 H, $J_{5,6a}$ 5.7, $J_{6a,6b}$ 11.8 Hz, H-6a), 3.71 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 3.82 (m, 1 H, $J_{4',5'}$ 9.7 Hz, H-5'), 4.17 (m, 1 H, $J_{4,5}$ 10.3 Hz, H-5), 4.75 (s, 1 H, $J_{1',2'}$ < 1Hz, H-1'), 5.01 (dd, 1 H, $J_{3',4'}$ 10.5 Hz, H-4'), 5.07 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.8 Hz, H-2), 5.09 (dd, 1 H, $J_{3,4}$ 9.7 Hz, H-4), 5.19 (d, 1 H, $J_{2',3'}$ 3.5 Hz, H-2'), 5.20 (dd, 1 H, H-3'), 5.55 (dd, 1 H, H-3), 6.49 (d, 1 H, H-1), and 8.74 (s, 1 H, NH); ^{13}C-n.m.r. ($CDCl_3$): δ 17.4 (C-6'), 20.4–20.9 (CH_3CO), 65.9 (C-6), 66.7 (C-5'), 68.6, 68.9 (C-4,3'), 69.6 (C-2'), 69.9, 70.0 (C-2,3), 71.1 (C-4'), 71.5 (C-5), 90.8 (CCl_3), 92.7 (C-1), 98.0 (C-1'), 160.6 (CNH), and 169.5–170.0 (CH_3CO).

A solution of **9** (0.6 g, 0.84 mmol) in anhydrous benzene (5 mL) was lyophilized in a 25-mL flask, and the residue dissolved in anhydrous dichloromethane (3 mL). Nerol (520 mg, 3.3 mmol) was added to the solution and the flask was sealed with a screw-cap septum and a Teflon disk. The mixture was stirred at 0°, and a 0.5M solution of boron trifluoride etherate (0.08 mmol) in dichloromethane (75 μL) wad added with a syringe through the septum during 20 min. The mixture was stirred for 2 h at room temperature, and then K_2CO_3 (50 mg, 0.36 mmol) and dichloromethane (10 mL) were added. The mixture was successively washed with water (25 mL), aqueous $NaHCO_3$ (25 mL), and water (25 mL). The organic layer was dried (Na_2SO_4) and concentrated. The crude residue was subjected to column chromatography (63–200 μm) with solvent *A* to elute the excess of nerol and solvent *D* to give **12** (357 mg, 0.50 mmol; 60%), syrup, $[\alpha]_D^{20}$ −3.6° (*c* 0.47, chloroform), R_F 0.53 (*D*).

Anal. Calc. for $C_{34}H_{50}O_{16}$: C, 57.13; H, 7.05. Found: C, 56.90; H, 6.87.

*Neryl 6-*O*-α-L-rhamnopyranosyl-β-D-glucopyranoside* (**26**). — Sodium methoxide (25 mg, 0.46 mmol) was added at room temperature to a solution of **12** (0.3 mmol) in

methanol (2 mL). The mixture was stirred and monitored by analytical t.l.c. (*J*) until disappearance of **12**. The base was neutralized with Amberlite IR ($^+$H) cation-exchange resin. Filtration and concentration gave **26** (97%), syrup, $[\alpha]_D^{20}$ −3.8° (*c* 0.27, methanol), R_F 0.53 (*K*).

Anal. Calc. for $C_{22}H_{38}O_{10}$: C, 57.13; H, 8.28. Found: C, 56.82; H, 7.89.

(R,S)-*Linalyl 6*-O-α-L-*rhamnopyranosyl*-β-D-*glucopyranoside* (**27**). — (*R,S*)-Linalyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranoside (**13**) was prepared from trichloroacetimidate **9** (0.73 mmol) and (±)-linalool (7.3 mmol) according to the procedure described for the preparation of **12**, except for the amount of boron trifluoride etherate (140 μL of a 0.1 M solution in anhydrous dichloromethane) added to the mixture. Column chromatography (43–60 μm) with solvent *A* eluted the excess of linalool and solvent *F* gave **13** (48%) as an oily residue, $[\alpha]_D^{20}$ −4.2° (*c* 0.41, chloroform), R_F 0.48 (*F*). Sodium methoxide treatment of **13**, as just described for the preparation of **26**, gave **27** (96%), syrup, $[\alpha]_D^{20}$ −3.5° (*c* 0.29, methanol), R_F 0.47 (*K*).

Anal. Calc. for $C_{22}H_{38}O_{10}$: C, 57.13; H, 8.28. Found: C, 56.75; H, 8.85.

(R,S)-α-*Terpinyl 6*-O-(α-L-*rhamnopyranosyl*)-β-D-*glycopyranoside* (**28**). — The hexaacetate **14** was prepared from the trichloroacetimidate **9** and (±)-α-terpinol as described for the preparation of **13** in 52% yield, oil, $[\alpha]_D^{20}$ −5.8° (*c* 0.37, chloroform), R_F 0.53 (*D*). Sodium methoxide treatment of **14** gave **28** (96%), syrup, $[\alpha]_D^{20}$ −3.8° (*c* 0.42, methanol), R_F 0.45 (*K*).

Anal. Calc. for $C_{22}H_{38}O_{10}$: C, 57.13; H, 8.28. Found: C, 56.82; H, 8.64.

Benzyl 6-O-α-L-*rhamnopyranosyl*-β-D-*glucopyranoside* (**29**). — Treatment of the trichloroacetimidate **9** with benzyl alcohol, as described for the preparation of **12**, gave benzyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranoside (**15**) in 71% yield, white powder, $[\alpha]_D^{20}$ −6.8° (*c* 0.76, chloroform), R_F 0.33 (*F*). Preparation of **15** from 2,3,4,2′,3′,4′-hexa-*O*-acetyl-α-rutinosyl bromide (**4**) and benzyl alcohol according to Baumes *et al.*[12] gave a 22% yield. Sodium methoxide treatment of **15** afforded **29** (98%), white powder, $[\alpha]_D^{20}$ −6.5° (*c* 0.34, methanol), R_F 0.46 (*K*).

Anal. Calc. for $C_{19}H_{28}O_{10}$: C, 54.80; H, 6.78. Found: C, 55.12; H, 6.82.

2-Phenylethyl 6-O-α-L-*rhamnopyranosyl*-β-D-*glucopyranoside* (**30**). — Treatment of the trichloroacetimidate **9** with 2-phenylethanol, as described for the preparation of **12**, gave 2-phenylethyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranoside (**16**) in 68% yield, white powder, $[\alpha]_D^{20}$ −5.2° (*c* 0.41, chloroform), R_F 0.32 (*F*). Preparation of **16** from **4** and 2-phenylethanol according to Baumes *et al.*[12] gave a 19% yield. Sodium methoxide treatment of **16** afforded **30** (98%), white powder, $[\alpha]_D^{20}$ −4.5° (*c* 0.33, methanol), R_F 0.45 (*K*).

Anal. Calc. for $C_{20}H_{30}O_{10}$: C,55.81; H, 7.03. Found; C, 55.82; H, 7.26.

Geranyl 2,3,4-tri-O-*acetyl-6*-O-*(2,3,5-tri*-O-*acetyl*-α-L-*arabinofuranosyl)*-β-D-*glucopyranoside* (**18**). — 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-α,β-D-glucopyranose (**7, 8**) was prepared from 1,2,3,4-tetra-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranose[16] (**2**; 1.98 mmol) as described for the preparation of **5** and **6**. The crude residue obtained was subjected to column chromatography (63–200 μm; solvent *D*) to give **7** and **8** as a syrup (932 mg, 1.65 mmol,

83%; (832 mg, 1.47 mmol) ratio **7** to **8** in $CDCl_3$, 3:1), R_F 0.3 (*F*). Treatment of the mixture, as described for the preparation of **9**, gave crude 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-α-D-glucopyranosyl trichloracetimidate (**10**) Column chromatography (63–200 μm, solvent *D*) gave **10** as a yellow oil (1 g, 1.41 mmol, 96%), R_F 0.4 (*D*); ^{1}H-n.m.r.: δ 2.00–2.15 (6 s, 18 H, 6 AcO), 3.62 (dd, 1 H, $J_{5,6a}$, 4.5, $J_{6a,6b}$ 11.7 Hz, H-6a), 3.81 (dd, 1 H, $J_{5,6b}$ 2.1 Hz, H-6b), 4.16–4.36 (m, 3 H, H-5,4',5'a), 4.40 (dd, 1 H, $J_{4',5'b}$ 2.9, $J_{5'a,5'b}$ 11.3 Hz, H-5'b), 4.83–5.31 (m, 4 H, H-2,4,2',3'), 5.07 (s, 1 H, $J_{1',2'} < 1$ Hz, H-1'), 5.56 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 9.9 Hz, H-3), 6.56 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), and 8.70 (s, 1 H, NH); ^{13}C-n.m.r., δ 20.4–20.7 (CH_3CO), 63.4 (C-5'), 65.7 (C-6), 68.5 (C-4), 70.0, 70.2 (C-2, C-3), 71.5 (C-5), 77.2 (C-3'), 80.7 (C-4'), 81.3 (C-2'), 91.6 (CCl_3), 93.3 (C-1), 106.2 (C-1'), 161.1 (CNH), and 169.3–170.7 (CH_3CO).

Condensation of the trichloroacetimidate **10** with geraniol, as described for the preparation of **12**, gave after column chromatography (solvent *B* and then *F*) **18** (61%) as an oily residue, $[\alpha]_D^{20}$ −3.1° (*c* 1.2, chloroform), R_F 0.49 (*D*).

Anal. Calc. for $C_{33}H_{48}O_{16}$: C, 56.56; H, 6.90. Found: C, 56.25; H, 7.38.

Geranyl 6-O-α-L-arabinofuranosyl-β-D-glucopyranoside (**32**). — This compound was prepared from **18** as described for the preparation of **26** (97%), syrup, $[\alpha]_D^{20}$ −7.9° (*c* 0.71, methanol), R_F 0.44 (*K*).

Anal. Calc. for $C_{21}H_{36}O_{10}$: C, 56.24; H, 8.09. Found: C, 56.42; H, 8.51.

Neryl 6-O-α-L-arabinofuranosyl-β-D-glucopyranoside (**33**). — Neryl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranoside (**19**) was prepared from trichloroacetimidate **10** and nerol as described for the preparation of **18**. Column chromatography (solvent *B* and then *F*) gave **19** (55%) as an oily residue, $[\alpha]_D^{20}$ −2.9° (*c* 1.1, chloroform), R_F 0.28 (*F*). Sodium methoxide treatment gave **33** (96%), syrup, $[\alpha]_D^{20}$ −7.1° (*c* 0.31, methanol), R_F 0.45 (*K*).

Anal. Calc. for $C_{21}H_{36}O_{10}$: C, 56.24; H, 8.09. Found: C, 56.53; H, 8.46.

(R,S)-*Linalyl 6-O-α-L-arabinofuranosyl-β-D-glucopyranoside* (**34**). — (*R,S*)-Linalyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranoside (**20**) was prepared from trichloroacetimidate **10** and (±)-linalool as described for the preparation of **13**. Column chromatography (40–63 μm, solvent *H*) gave **20** (65%) as an oily residue, $[\alpha]_D^{20}$ −4.3° (*c* 1.0, chloroform), R_F 0.37 (*F*). Sodium methoxide treatment of **20** gave **34** (96%), syrup, $[\alpha]_D^{20}$ −4.9° (*c* 0.35, methanol), R_F 0.47 (*K*).

Anal. Calc. for $C_{21}H_{36}O_{10}$: C, 56.24; H, 8.09. Found: C, 56.60; H, 8.51.

(R,S)-α-*Terpinyl 6-O-(α-L-arabinofuranosyl-β-D-glucopyranoside* (**35**). — (*R,S*)-α-Terpinyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranoside (**21**) was prepared from trichloroacetimidate **10** and (±)-α-terpineol as described for the preparation of **20**. Column chromatography (63–200 μm; solvent *G*) gave **21** (48%) as an oily residue, $[\alpha]_D^{20}$ −4.1° (*c* 1.2, chloroform), R_F 0.29 (*F*). Sodium methoxide treatment of **21** gave **35** (96%), syrup, $[\alpha]_D^{20}$ −5.5° (*c* 0.29, methanol), R_F 0.44 (*K*).

Anal. Calc. for $C_{21}H_{36}O_{10}$: C, 56.24; H, 8.09. Found: C, 55.98; H, 7.91.

Benzyl 6-O-α-L-arabinofuranosyl-β-D-glucopyranoside (**36**). — Benzyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranoside (**22**) was

prepared from trichloroacetimidate **10** and benzyl alcohol as described for the preparation of **18**. Column chromatography (63–200 μm, solvent *A* and then *I*) gave, after cristallization from diethyl ether, **22** (83%), m.p. 113–114°, $[\alpha]_D^{20}$ −6.6° (*c* 1.2, chloroform), R_F 0.24 (*F*). Sodium methoxide treatment of **22** gave **36** (98%), white powder, $[\alpha]_D^{20}$ −9.8° (*c* 0.58, methanol), R_F 0.48 (*K*).

Anal. Calc. for $C_{18}H_{26}O_{10}$: C, 53.73; H, 6.51. Found: C, 54.04; H, 6.86.

2-Phenylethyl 6-O-α-L-arabinofuranosyl-β-D-glucopyranoside (**37**). — 2-Phenylethyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranoside (**23**) was prepared from trichloroacetimidate **10** and 2-phenylethanol as described for the preparation of **18**. Crystallization from diethyl ether gave **23** (76%), m.p. 102–103°, $[\alpha]_D^{20}$ −4.5° (*c* 1.2, chloroform), R_F 0.27 (*F*). Sodium methoxide treatment of **23** gave **37** (98%), white powder, $[\alpha]_D^{20}$ −7.6° (*c* 0.29, methanol), R_F 0.43 (*K*).

Anal. Calc. for $C_{19}H_{28}O_{10}$: C, 54.80; H, 6.78. Found: C,54.53; H, 6.66.

4-Nitrophenyl 6-O-α-L-arabinofuranosyl-β-D-glucopyranoside (**38**). —(*a*). 4-Nitrophenyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranoside (**24**) was prepared from trichloroacetimidate **10** and 4-nitrophenol as described for the preparation of **18**. Crystallisation from methanol–diethyl ether gave **24** (68%), m.p. 176–177°, $[\alpha]_D^{20}$ −8° (*c* 0.58, chloroform), R_F 0.24 (*F*).

(*b*). Chlorotriphenylmethane (5.4 mmol) was added portionwise with stirring to a solution of 4-nitrophenyl β-D-glucopyranoside (4.7 mmol, Sigma) in pyridine (10 mL). The mixture was kept for 24 h at 40°, and then treated with acetic anhydride (6 mL), kept for 48 h at room temperature, and then treated with water (500 mL) for 2 h. Dichloromethane (100 mL) was added and the mixture filtered. The organic layer was washed with water, aqueous HCl, aqueous $NaHCO_3$, water, and concentrated. Column chromatography of the crude residue (63–200 μm, solvent *C*) gave 4-nitrophenyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**44**; 3.9 mmol, 83%), syrup, R_F 0.33 (*C*); ^{13}C-n.m.r. ($CDCl_3$): δ 20.4, 20.6 (*C*H_3CO), 62.4 (C-6), 68.8 (C-4), 71.5 (C-2), 73.0 (C-3), 74.5 (C-5), 87.4 (*C*Ph_3), 98.6 (C-1), 117.1, 125.9, 143.7, 161.7 (4-$NO_2C_6H_4$), 127.4, 128.1, 128.5, 128.9 [C(*C*$_6H_5$)$_3$], 169.2, 169.4, and 170.3 (CH_3*C*O).

The crude residue obtained from 3,5-di-*O*-acetyl-1,2-*O*-[(1-*exo*- and 1-*endo*-cyano)ethylidene]-β-L-arabinofuranoses[16] (0.5 mmol) and 4-nitrophenyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**44**; 0.55 mmol) according to the procedure described by Backinowsky *et al.*[16] for the synthesis of **2**, was subjected to column chromatography (63–200 μm, solvent *F*) to give **24** (12%) and 4-nitrophenyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,5-tri-*O*-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranoside (**39**; 10%), syrup, $[\alpha]_D^{20}$ −64° (*c* 1.0, chloroform), R_F 0.28 (*F*); ^{1}H-n.m.r. ($CDCl_3$): δ 2.05–2.14 (6 s, 18 H, 6 AcO), 3.85 (m, 1 H, $J_{4,5}$ 9.0, $J_{5,6a}$ 4.4, $J_{5,6b}$ 1.6 Hz, H-5), 3.89 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-4), 4.16 (dd, $J_{4',5'a}$ 5.7, $J_{5'a,5'b}$ 11.0 Hz, H-5'a), 4.20 (m, $J_{3',4'}$ 4.8, $J_{4',5'b}$ 2.6 Hz, H-4'), 4.31 (dd, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.38 (dd, $J_{4',5'b}$ 2.5 Hz, H-5'b), 4.51 (dd, H-6b), 4.99 (m, 2 H, H-2',3'), 5.04 (s, 1 H, $J_{1',2'}$ < 1 Hz, H-1'), 5.19 (d, $J_{1,2}$ 6 Hz, H-1), 5.30 (m, 2 H, H-2,3), 7.07 (m, 2 H, arom.), and 8.21 (m, 2 H, arom.); ^{13}C-n.m.r.: δ 20.6, 20.7, 20.9 (*C*H_3CO), 62.2 (C-6), 63.2 (C-5'),71.7 (C-2), 73.3, 73.6 (C-3,5), 76.4, 76.6 (C-3',4), 81.5 (C-4'), 81.9 (C-2'), 98.3 (C-1), 107.8 (C-1'), 116.9, 125.9, 143.6, 161.5 (arom.), and 169.5, 170.0, 170.3, 170.4, 170.6 (CH_3*C*O).

Sodium methoxide treatment of **24** gave **38** (97%), yellow powder, $[\alpha]_D^{20}$ $-12°$ (*c* 0.45, methanol), R_F 0.7 (*J*).

Anal. Calc. for $C_{17}H_{23}NO_{12}$: C, 47.12; H, 5.35; N, 3.23. Found: C, 47.43; H, 5.10; N, 3.07.

O-Deacetylation of 1,2,3,4-tetra-O-acetyl-6-O-(2,3,5-tri-O-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranose (**2**). — Compound[16] **2** was deacetylated as described for the preparation of **26** to give 6-*O*-(α-L-arabinofuranosyl)-α,β-D-glucopyranose (**42** and **43**; 98%), yellow powder, $[\alpha]_D^{20}$ $-4.4°$ (*c* 0.57, methanol), R_F 0.33 (methanol); ^{1}H-n.m.r. (D_2O): δ 2.88 (dd, 1 H, $J_{1,2}$ 7.7, $J_{2,3}$ 8.6 Hz, H-2β), 2.97 (m, 2 H, $J_{3,4} \sim J_{4,5} \sim 8.8$ Hz, H-4α,4β), 3.10 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.3 Hz, H-2α), 3.11 (dd, 1 H, $J_{2,3} \sim J_{3,4} \sim 9.0$ Hz, H-3β), 4.26 (d, 1 H, H-1β), 4.71 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1'α), 4.72 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1'β), 4.87 (d, 1 H, H-1α), and other signals between 3.22–3.87; ^{13}C-n.m.r.: δ 62.0 (C-5'α,5'β), 67.8 (C-6α,6β), 70.6 (C-4α,4β), 71.2 (C-5α), 72.3 (C-2α), 73.5 (C-3α), 74.9 (C-2β), 75.5 (C-3β), 76.5 (C-5β), 77.3 (C-3'α,3'β), 81.7, 81.8 (C-2'α,2'β), 84.4, 84.6 (C-4'α,4'β), 92.9 (C-1α), 96.8 (C-1β), and 108.9 (C-1'α,1'β).

REFERENCES

1 R. Cordonnier and C. Bayonove, *C.R. Hebd. Seances Acad. Sci. Paris, Ser. D*, 278 (1975) 3387–3392.
2 C. R. Straus, B. Wilson, P. R. Gooley, and P. J. Williams, *ACS Symp. Ser.*, 317 (1986) 222–242, and references cited herein.
3 Y. Z. Gunata, Thèse de Docteur-Ingénieur, Université des Sciences et Techniques du Languedoc, Montpellier, 1984.
4 P. J. Williams, C. R. Strauss, B. Wilson, and R. A. Massy-Westropp, *Phytochemistry*, 21 (1982) 2013–2020.
5 P. J. Williams, C. R. Strauss, B. Wilson, and R. A. Massy-Westropp, *Phytochemistry*, 22 (1983) 2039–2041.
6 C. R. Strauss, Thesis, University of Adelaide, South Australia, 1983.
7 B. Wilson, C. R. Strauss, and P. J. Williams, *J. Agric. Food Chem.*, 32 (1984) 919–924.
8 B. Wilson, C. R. Strauss, and P. J. Williams, *Am. J. Enol. Vitic.*, 37 (1986) 107–111.
9 C. R. Strauss, P. R. Gooley, B. Wilson, and P. J. Williams, *J. Agric. Food. Chem.*, 35 (1987) 519–524.
10 C. R. Strauss, B. Wilson, and P. J. Williams, *J. Agric. Food Chem.*, 36 (1988) 569–573.
11 Y. Z. Gunata, S. Bitteur, R. Baumes, J. M. Brillouet, C. Tapiero, C. Bayonove, and R. Cordonnier, *Fr. Pat. pending* (1988).
12 R. L. Baumes, C. L. Bayonove, R. E. Cordonnier, Y. Z. Gunata, R. Wylde and A. Heitz, *Carbohydr. Res.*, 189 (1989) 331–340.
13 R. Bourbouze, Thèse de Doctorat d'État, Université René Descartes de Paris, 1974.
14 F. Pierrisnard, Diplôme d'Études Approfondies en Sciences Alimentaires, Université des Sciences et Techniques du Languedoc, Montpellier, 1986.
15 M. K. Shakhova, G. I. Samokhvalov, and N. A. Preobrazhenskii, *Zh. Obshch. Khim.*, 32 (1962) 390–396.
16 L. V. Backinowsky, S. A. Nepogod'ev, A. S. Shashkov, and N. K. Kochetkov, *Carbohydr. Res.*, 138 (1985) 41–54.
17 R. R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 25 (1986) 212–235; and references cited herein.
18 J. Michel, Dissertation, Universität Konstanz, 1983.
19 J. Fiandor, M. T. Carcia-Lopez, F. G. de Las Heras, and P. P. Mendez-Castillon, *Synthesis*, (1985) 1121–1123.
20 P. Kováč and C. P. J. Glaudemans, *Carbohydr. Res.*, 140 (1985) 313–318.
21 L. V. Backinowsky, N. F. Balan, A. S. Shashkov, and N. K. Kochetkov, *Carbohydr. Res.*, 84 (1980) 225–235.
22 A. M. Nguyen Phuoc Du, Thèse de Doctorat de Spécialité, Université des Sciences et Techniques du Languedoc, Montpellier, 1986.

23 C. Lafitte, A. M. Nguyen Phuoc Du, F. Winternitz, R. Wylde, and F. Pratviel-Sosa, *Carbohydr. Res.*, 67 (1978) 91–103.
24 L. Huiying, L. Shouzhen, T. McCabe, and J. Clardy, *Planta Medica*, (1984) 501–504.
25 D. Y. Gagnaire, F. R. Taravel, and M. R. Vignon, *Carbohydr. Res.*, 51 (1976) 157–168.
26 K. Bock and C. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, (1974) 293–299.
27 B. L. Kam, J. L. Barascut, and J. L. Imbach, *Carbohydr. Res.*, 69 (1979) 135–142.
28 P. A. J. Gorin and M. Mazurek, *Can. J. Chem.*, 53 (1975) 1212–1223.
29 F. Bohlmann and M. Grenz, *Phytochemistry*, 16 (1977) 1057–1059.
30 F. Bohlmann, R. Zeisberg, and E. Klein, *Org. Magn. Reson.*, 7 (1975) 426–432.
31 A. A. Swigar and R. M. Silverstein, *Monoterpenes*, Aldrich Chem. Co., Inc., Milwaukee, Wisconsin, 1981.
32 O. M'Bairaroua, C. Tapiero, Voirin S., R. Baumes, and C. Bayonove, unpublished results.
33 C. T. Bishop and F. P. Cooper, *Can. J. Chem.*, 41 (1963) 2743–2758.
34 R. Kasai, M. Okihara, J. I. Asakawa, K. Mitzutani, and O. Tanaka, *Tetrahedron*, 35 (1979) 1427–1432.
35 K. Mizutani, R. Kasai, and O. Tanaka, *Carbohydr. Res.*, 87 (1980) 19–26.
36 R. Kasai, M. Suzuo, J. I. Asakawa and O. Tanaka, *Tetrahedron Lett.*, (1977) 175–178.
37 K. Tori, S. Seo, Y. Yoshimura, H. Arita, and Y. Tomita, *Tetrahedron Lett.*, (1977) 179–182.
38 H. Kizu, M. Koshijima, M. Hayashi, and T. Tomimori, *Chem. Pharm. Bull.*, 33 (1985) 1400–1406.
39 H. Kizu, M. Koshijima, and T. Tomimori, *Chem. Pharm. Bull.*, 33 (1985) 3176–3181.
40 E. Breitmaier, W. Voelter, G. Jung, and C. Tänzer, *Chem. Ber.*, 104 (1971) 1147–1154.
41 K. Tori, T. Hirata, O. Koshitani, and T. Suga, *Tetrahedron Lett.*, (1976) 1311–1314.
42 S. Nishibe, H. Tsukamoto, and S. Hisada, *Chem. Pharm. Bull.*, 32 (1984) 4653–4657.
43 S. Seo, Y. Tomita, K. Tori, and Y. Yoshimura, *J. Am. Chem. Soc.*, 100 (1978) 3331–3339.
44 IUPAC–IUB Joint Commission on Biochemical Nomenclature (JCBN), *Eur. J. Biochem.*, 131 (1983) 5–7.
45 R. U. Lemieux and S. Koto, *Tetrahedron*, 30 (1974) 1933–1944.
46 D. A. Rees and W. E. Schott, *J. Chem. Soc., B*, (1971) 469–479.