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Note

Unusual carbonate formation in saccharide synthesis

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In our continuous efforts to study monoterpenoïd heterosides of *Vitis vinifera* grapes and wines[1–4], we required (*E*-3,7-dimethyl-2,6-octadienyl) 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranoside (**1**) (geranyl β-rutinoside hexaacetate) as a reference compound. As the method used by Williams *et al.*[5] gives a poor yield, we attempted to prepare this compound under the experimental conditions described earlier by Bourbouze[6] to synthesize 4-nitrophenyl β-rutinoside hexaacetate (**2**), *i.e.*, condensation of 2,3,4,2′,3′,4′-hexa-*O*-acetyl-α-rutinosyl chloride (**3**) with *p*-nitrophenol in pyridine in the presence of silver carbonate and Drierite. However, this reaction, which starts from the *cis*-haloside **3** in the presence of a strongly nucleophilic solvent, could lead to an orthoester *via* pyridine and C-2 substituent participation by formation of a transient α-acyloxonium ion[7–9]. However, the product obtained (**4**) was neither **1** nor an orthoester as it gave, under deacylation conditions, geraniol and rutinose (**5**). Furthermore, it did not rearrange by acid catalysis in the presence of geraniol into a geranyl glycoside. Apart from the reaction with water or the production of the α anomer, the known side reactions in this type of glycosylation lead to products arising from the postulated acyloxonium ion[7–9], *e.g.*, alkyl acetate, alkyl ether, and alkyl glycoside with a free OH-2. The products resulting from the acetoxonium ion rearrangement with inversion at some glycosidic carbon atoms have never been observed in glycoside synthesis proceeding *via* the acetoxonium ion[8].

In order to compare **4** to the acetylated rutinosides **1** and **2**, these and their deacylated products **6**, **7**, and **8** were synthesized according to previously reported methods[5,6]. (In the synthesis of **1**, use of the Helferich catalyst and acetonitrile as solvent led, with a better yield, to a product having t.l.c., ^{1}H- and ^{13}C-n.m.r. properties identical with those published[5].) The observed ^{1}H-n.m.r. data for **4** (Tables I and II) were similar to those for **1**, except that the chemical shifts of H-1

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TABLE I

^{1}H-N.M.R. CHEMICAL SHIFTS FOR THE RUTINOSE DERIVATIVES **1–4, 6, 7,** AND **10**

Compound	*Solvent*	*Chemical shift (δ)*												
		D-*Glucose residue*							L-*Rhamnose residue*					
		H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*
1	$CDCl_3$	4.48	4.91	5.15	4.90	3.61	3.61	3.66	4.76	5.20	5.20	5.01	3.82	1.17
2	$CDCl_3$	5.18	5.26	5.31	5.02	3.89	3.59	3.73	4.68	5.18	5.26	5.04	3.80	1.16
3	$CDCl_3$	6.28	4.97	5.54	5.10	4.26	3.58	3.76	4.68	5.23	5.25	5.03	3.85	1.20
4	$CDCl_3$	5.51	5.04	5.18	5.01	3.79	3.68	3.70	4.69	5.18	5.18	4.98	3.83	1.14
	$(CD_3)_2SO$	5.84	4.92	5.44	4.94	4.34	3.60	3.69	4.79	5.10	5.04	4.87	3.84	1.12
6	$(CD_3)_2SO$–CF_3CO_2H	4.12	2.97	3.14	3.04	3.19	3.45	3.82	4.61	3.63	3.44	3.19	3.47	1.12
7	$(CD_3)_2SO$–CF_3CO_2H	4.75	4.69	5.21	4.88	3.82	3.42	3.61	4.54	3.60	3.42	3.18	3.42	1.13
10	$CDCl_3$	5.41	5.15	5.25	4.92	3.54	3.24	3.51	4.49	5.06	5.05	4.92	3.62	1.03

TABLE I *(continued)*

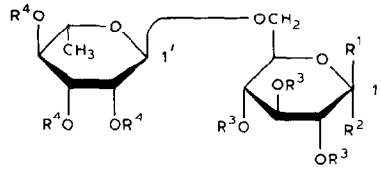
Compound	*Glycosidic acetates*	*Aglycon residue*												
		H-1	*H-1'*	*H-2*	*H-2'*	*H-3*	*H-4*	*H-5*	*H-5'*	*H-6*	*H-6'*	*H-8*	*Me-3*	*Me-7*	*Ac*
1	2.08–2 (×2) 1.98–1.95 1.93	4.14	4.20	5.20			1.93–2.08			5.04			1.64	1.56 1.61	
2	2.06 (×2) 2.05–2.04 2.02–2.01			7.04		8.24		8.24		7.04					
3	2.12–2.08 2.04–2.04 2.01–1.96														
4	2.07–2.00 1.99–1.97 1.95–1.92	4.64		5.30			1.92–2.07			4.98			1.65	1.53 1.64	
	2.09–2.03 2.01–2.00 1.95–1.91	4.65		5.32			1.93–2.09			5.06			1.68	1.56 1.64	
6		4.08	4.16	5.26			1.95–2.12			5.04			1.60	1.53 1.60	
7	1.99–1.98 1.93	4.09	4.17	5.21			1.95–2.11			5.07			1.65	1.58 1.62	
10	2.12–2.06 2.00 (×2) 1.93–1.92				7.88				7.32	6.82	7.93	7.28			2.42–2.32 2.31–2.27

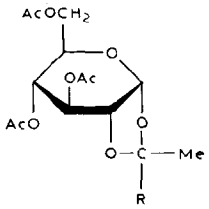
TABLE II

^{1}H-N.M.R. FIRST-ORDER COUPLING CONSTANTS FOR THE RUTINOSE DERIVATIVES **1–4, 6, 7,** AND **10**

Compound[a]	*Solvent*	*Coupling constant (Hz)*																			
		D-*Glucose residue*							L-*Rhamnose residue*					*Aglycon residue*							
		$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{2',5'}$	$J_{2',6'}$	$J_{5,6}$	$J_{5',6'}$	$J_{6,8}$
1	$CDCl_3$	8.1	9.5	9.5	9.5		1.9	9.3	0.9		9.7	9.7	6.3	12	7.9	6.2						
2	$CDCl_3$	6.9	9.3	9.4	9.7	7.5	2.3	11.5	1.4	3.8	9.9	9.8	6.3				9.2			9.2		
3	$CDCl_3$	4.0	9.9	9.7	9.9	4.8	2.3	11.9	<1	3.5	9.7	9.8	6.2									
4	$CDCl_3$	7.8	9.3	9.8	9.8	5.5	2.7	11.9	<1		9.8	9.8	6.2		6.9							
	$(CD_3)_2SO$	8.5	9.2	9.4	9.4	6.8	2.0	12.0	1.1	3.4	10.1	9.7	6.5		7.6							
6	$(CD_3)SO$–CF_3CO_2H	7.8	8.4	8.9	9.2		1.5	11.2	1.3	3.5	9.9		6.2	11.7	8.0	6.0						
7	$(CD_3)SO$–CF_3CO_2H	7.0	7.6	9.8	9.8		1.0	13.0	<1		9.5	9.5	6.5	12.5	7.0	7.0						
10	$CDCl_3$	7.8	9.5	9.5	9.5	5.5	3.2	10.8	<1	3.5	9.5	9.5	6.3					<0.5	2.1		8.6	2.2

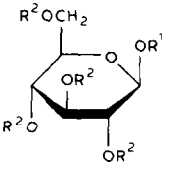
[a]The coupling constants between the geranyl H-4,5,6 in **1, 4, 6,** and **7** were not determined. Other coupling constants between the 4-nitrophenyl group protons in **2** are ~0 Hz.



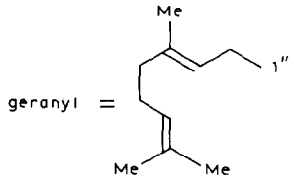


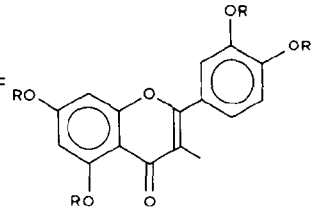
1 R^1 = Ogeranyl, R^2 = H, R^3 = R^4 = Ac
2 R^1 = O-(4-nitrophenyl), R^2 = H, R^3 = R^4 = Ac
3 R^1 = H, R^2 = Cl, R^3 = R^4 = Ac
4 R^1 = OCO_2geranyl, R^2 = H, R^3 = R^4 = Ac
5 R^1 = R^2 = H,OH; R^3 = R^4 = H
6 R^1 = Ogeranyl, R^2 = R^3 = R^4 = H
7 R^1 = Ogeranyl, R^2 = R^4 = H, R^3 = Ac
8 R^1 = O-(4-nitrophenyl), R^2 = R^3 = R^4 = H
9 R^1 = R^3 = R^4 = Ac, R^2 = H
10 R^1 = O-quercetinyl tetraacetate, R^2 = H, R^3 = R^4 = Ac
11 R^1 = O-quercetinyl, R^2 = R^3 = R^4 = H
12 R^1 = H, R^2 = Br, R^3 = R^4 = Ac

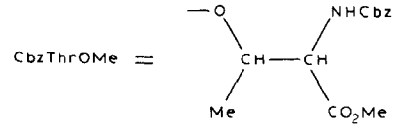
13 R = CbzThrOMe
14 R = $C_6H_{11}(CH_2)$-O-



15 R^1 = CO_2Me, R^2 = Ac
16 R^1 = R^2 = Ac







(D-glucosyl) and H-1 (geranyl) were at a much lower field than comparable signals for **1**. The deshielding of both latter protons is strongly indicative of a deshielding residue between the sugar and terpene units. The other observed signals were consistent with the presence of a hexa-*O*-acetyl-β-rutinosyl residue[10] and a geranyl residue as the aglycon. Moreover, the chemical shift of the signal for H-1 of **4** was close to that observed for H-1 of the D-glucose α-orthoesters **13** (ref. 11) and **14** (ref. 12), and of 2,3,4,6-tetra-*O*-acetyl-1-*O*-methoxycarbonyl-β-D-glucopyranose[12] (**15**). However, the observed coupling constants for H-1 to H-6 of **4** suggested a normal $^4C_1$(D) conformation with a β-D configuration, in contrast to the orthoesters **13** and **14**. In addition, the chemical shifts of the signals for H-2 and the methyl

TABLE III

^{13}C-N.M.R. CHEMICAL SHIFTS FOR THE RUTINOSE DERIVATIVES **1–4**[a]

Chemical shifts (δ)	*Compound*			
	1[b]	**2**	**3**	**4**
D-*Glucose residue*				
C-1	98.8	98.0[c]	90.1[e]	94.7[g]
C-2	71.0	70.8	69.6	70.1
C-3	73.0	72.5	71.1	72.6
C-4	68.9	68.8[d]	68.9	68.5[h]
C-5	73.3	73.9	71.3	73.6
C-6	66.6	66.7	66.3	66.6
L-*Rhamnose residue*				
C-1	98.2	98.2[c]	98.3	98.0[i]
C-2	70.2	69.3	69.5	69.4
C-3	68.7	68.9[d]	68.1	68.7[h]
C-4	70.9	71.1	70.9	70.8
C-5	67.3	66.9	66.7	66.4
C-6	17.5	17.4	17.4	17.4
Aglycon residue				
C-1	65.2	161.0		65.3
C-2	119.3	116.5		116.9
C-3	142.5	126.0		143.5
C-4	39.5	143.4		39.2
C-5	26.2	126.0		26.0
C-6	122.3	116.5		123.3
C-7	131.8			131.5
Me-3	16.2			16.2
Me-7-*cis*	17.3			17.1
Me-7-*trans*	25.5			25.4
CH_3CO	20.4–20.6	20.6–20.7	20.5–20.7	20.2–20.5
CH_3CO	169.4–170.4	169.1–170.1	169.3–170.0	168.7–169.8
CO_3				153.1

[a]For a solution in (^{2}H)chloroform. [b]See ref. 5. [c,d,h]Assignments may be interchanged. [e]$J_{^{13}C,H\text{-}1}$ 184.6 Hz. [f]$J_{^{13}C,H\text{-}1}$ 171.3 Hz. [g]$J_{^{13}C,H\text{-}1}$ 169 Hz. [i]$J_{^{13}C,H\text{-}1}$ 171 Hz.

orthoester group of an orthoester structure would be in the range[11,12] of δ 4.3–4.4 and 1.6–1.8, respectively. The β-D configuration of C-1 of **4** was confirmed by the solvent effect observed between solutions in $CDCl_3$ and $(CD_3)_2SO$, resulting in a downfield shift of the signals for H-1, H-3, and H-5, and in an upfield shift of those for H-2, H-4, and H-6.

The ^{13}C-n.m.r. spectrum of **4** (Table III) further supported the carbonate structure of the β-D anomer suggested by the ^{1}H-n.m.r. study. Firstly, the chemical shifts of the signals for the carbon atoms of **4** were in good agreement with those for **1** and **2**, except for that of C-1 being at a higher field not far from the range of values reported for β-rutinose heptaacetate[14] (**9**) and for β-D-glucopyranose pentaacetate[15] (**16**). Secondly, the signal for an extra nonprotonated carbon atom in **4** was present at δ 153.1, which is compatible with the carbonyl group of a carbonate

residue but excludes an orthoester residue[11]. The coupling constant between C-1 and H-1 in **4** was 169 Hz, an increase of ~8 Hz relative to that of alkyl β-D-glucopyranoside tetraacetates[16]. This increase for **4** is probably due to the electronegativity of the carbonate residue at C-1 (*c.f.*, the characteristic $J_{C\text{-}1,H\text{-}1}$ 184.6 Hz for the α-chloride **3**) and the probable presence of neighboring lone electron pairs of the carbonate residue close to H-1 (ref. 16).

These deductions were confirmed by the presence of broad bands at 1765 and 1240 cm^{-1} in the i.r. spectrum of **4** (respectively carbonyl and C–O stretching bands of both acetate and carbonate groups[12]), by the similarity between the e.i. mass spectra of **1** and **4**, which showed significant fragment ions at *m/z* 561 ($C_{24}H_{33}O_{15}$, rhamnoglucosyl hexaacetate residue), 273 ($C_{12}H_{17}O_7$, terminal rhamnosyl triacetate residue), 153,69, 111,81, 136, 68, and 93 (geranyl residue), and by the formation of geraniol and rutinose (**5**) from **4** under deacylation conditions. It should be noted that **1** and **2** are completely deacetylated under the same conditions. In the case of **1**, a trace of a partial *O*-deacetylated rhamnose-containing product **7** was also isolated and it yielded **6** after a longer hydrolysis time.

Therefore, we propose carbonate structure **4** for the compound obtained by condensation of **3** with geraniol in pyridine in the presence of silver carbonate. It is of interest that 4-nitrophenol, under the same conditions, led to the 4-nitrophenyl β-rutinoside hexaacetate (**2**). This different result may be explained by the formation, in the latter case, of a reactive species towards the sugar chloride by the silver salt of 4-nitrophenol and silver carbonate in a coordinating aprotic solvent, like pyridine. In contrast, geraniol would form preferentially in this solvent a silver geranyl carbonate[17,18], which would be the reactive species. The excellent solvating properties of coordinating aprotic solvent, for related metal alkyl carbonates have been described previously[17,18].

However, in the case of **2**, the possible formation of an unstable 4-nitrophenoxycarbonyl β-rutinoside hexaacetate reacting with an excess of 4-nitrophenol to give **2** cannot be excluded, although the conditions used in the present work are not as harsh as those used in the case of carbonate activation[12,19,20].

EXPERIMENTAL

General methods. — Optical rotations were measured with a Perkin–Elmer 241 polarimeter at 21°. N.m.r. spectra were recorded with a Bruker 360 MHz spectrometer (360 MHz for ^{1}H-n.m.r. and 90.56 MHz for ^{13}C-n.m.r.) for solutions in (^{2}H)chloroform or di($^2H_3$)methyl sulfoxide (internal standard, tetramethylsilane). ^{1}H-resonance assignments were made by use of conventional decoupling techniques. ^{1}H- and ^{13}C-coupling constants were measured on spectra obtained by gated-decoupling techniques. E.i.m.s. and f.a.b.m.s. were recorded with a Jeol DX 300 instrument; e.i.m.s. scanning at 70 eV from *m/z* 30 to 1000 and positive f.a.b.m.s. in glycerol with Xe (energy 3 Kev). Column chromatography was performed on Silica Gel 60 (Merck, 70–230 mesh) and t.l.c. on Silica Gel 60 (Merck)

with detection by charring with H_2SO_4. The following solvent systems were used: (*A*) 4:1 ether–petroleum ether, (*B*) 3:1 ether–petroleum ether, (*C*) 1:1 ether–petroleum ether, (*D*) 3:1 ethyl acetate–ethanol, (*E*) 4:1 toluene–acetone, and (*F*) 13:6:2 ethyl acetate–2-propanol–water. Analytical g.l.c. was performed in a CPWAX 52CB fused-silica capillary column (Chrompack, 25 m × 0.32 mm i.d.) in a Varian 3700 gas chromatograph fitted with f.i.d. The temperature of the on-column Varian injector was programmed at 180°/min from 20 to 250°, and then was held at 250°; the detector temperature was at 250°; and the oven temperature was programmed at 2°/min from 70 to 180° with 2.5 mL/min; H_2 was the carrier gas. Compounds **2, 3, 8,** and **10** were synthesized from rutin (**11**) by the method of Bourbouze[6].

2,3,4-Tri-O-acetyl-1-O-geranyloxycarbonyl-6-O-(2,3,4-tri-O-acetyl-6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranose (**4**). — Drierite (14.7 mmol) and geraniol (5.2 mmol) were stirred for 1 h in anhydrous pyridine (20 mL) and then 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-α-L-mannopyranosyl)-α-D-glucopyranosyl chloride[6] (**3**, 2.4 mmol) and freshly prepared Ag_2CO_3 (3.6 mmol) were added. The mixture was stirred in the dark for 8 days at room temperature and then filtered and the filtrate concentrated *in vacuo*. The crude product was dissolved in benzene (100 mL) and the solution washed with ice-cold water, with M NaOH, again with ice-cold water, and dried (Na_2SO_4). After filtration and concentration, the oily residue was subjected to column chromatography (solvent *A*) to give **4** as foam (0.3 mmol, 13%); $[\alpha]_D^{21}$ −4.07° (*c* 0.54, chloroform); R_F 0.43 (solvent *A*), 0.55 (solvent *E*); e.i.m.s.: *m/z* 153 (100), 69 (98), 111 (94), 273 (71), 81 (55), 171 (39), 93 (35), 136 (32), 68 (32), 83 (28), 137 (25), 213 (23), 115 (21), 127 (21), 109 (19), 157 (19), and 97 (17); other significant fragment ions at: *m/z* 317 (2.2), 289 (1.8), 331 (0.4), and 561 (0.05).

Anal. Calc. for $C_{35}H_{50}O_{18}$: C, 55.40; H, 6.64. Found: C, 55.96; H, 7.27.

Deacylation of compound **4**. — 0.1M Sodium methoxide in methanol (0.3 mL, 0.03 mmol) was added at room temperature to **4** (0.26 mmol) dissolved in methanol (2 mL) under N_2. The mixture was stirred for 20 min at 68–70°. After cooling, addition of Dowex 50W-X4 (H^+, 0.2 mL) resin (to neutrality) and filtration, the mixture was concentrated *in vacuo*. Geraniol (R_F 0.63, solvent *E*) was extracted with ether from the crude residue consisting mainly of rutinose (**5**; R_F 0.10, solvent *F*). The identity of geraniol was confirmed by comparison of its ^{1}H-n.m.r. and g.l.c. properties with those of an authentic sample, and that of rutinose (**5**) by its ^{1}H-n.m.r. spectrum.

Geranyl 2,3,4-tri-O-acetyl-6-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranoside [*(E-3,7-dimethyl-2,6-octadienyl) 2,3,4-tri-O-acetyl-6-O-(2,3,4-tri-O-acetyl-6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranoside; geranyl β-rutinoside hexaacetate;* **1**]. — A mixture of 2,3,4,2′,3′,4′-hexa-*O*-acetyl-α-D-rutinopyranosyl bromide[5] (**12**; 1 mmol), geraniol (5.8 mmol), and $Hg(CN)_2$ (2 mmol) was stirred in acetonitrile (10 mL) for 24 h at room temperature. The mixture was concentrated *in vacuo*, and then ether (50 mL) was added. The insoluble mass was

filtered off and washed with ether (10 mL). The oily residue obtained after concentration of the filtrate was subjected to column chromatography (solvent *C*, and then solvent *B*) to give syrupy **1** (0.19 mmol, 19%); $[\alpha]_D^{21}$ −4.9° (*c* 2.5, chloroform); R_F 0.33 (solvent *B*), R_F 0.45 (Solvent *E*); ^{1}H-n.m.r., see Tables I and II; ^{13}C-n.m.r., see Table III; e.i.m.s.: *m/z* 69 (100), 153 (96), 111 (88), 273 (70), 81 (55), 136 (46), 68 (33), 171 (32), 93 (30), 137 (30), 139 (29), 83 (25), 109 (20), 213 (19), 127 (18), and 97 (17); other significant fragment ions at *m/z* 317 (5.5), 289 (3.3), 331 (1.1), 561 (0.7), and 577 (0.1); lit.[5] syrup, R_F 0.44 (solvent *E*); ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 1.15 (d, 3 H, *J* 6.3 Hz, H-6′), 1.55 (s, 3 H, geranyl Me-7), 1.59 (s, 6 H, geranyl Me-3 and Me-7), 2.0 (m, 22 H, 6 AcO, geranyl H-4a,4b,5a,5b), 3.69 (m, 4 H, H-5,6a,6b,5′), 4.16 (d, 2 H, *J* 6.8 Hz, geranyl H-1), 4.47 (d, 1 H, *J* 7.5 Hz, H-1), 4.70–5.48 (m, 9 H, H-2,3,4,1′,2′,3′,4′, geranyl H-2,6); e.i.m.s. (20 eV): *m/z* 136 (100), 153 (94), 273 (78), 93 (63), 111 (45), 43 (41), 139 (33), 81 (32), 69 (30), 137 (29), 92 (22), 213 (21), 171 (20), 122 (20), 121 (19), 123 (16), 157 (15), 184 (15), 274 (11), 109 (11), 317 (5), and 289 (2).

The remaining reaction mixture consisted mainly of hydrolysis products of **12**, *i.e.*, 2,3,4-tri-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α- and -β-D-glucopyranose, R_F 0.31 (solvent ether); ^{1}H-n.m.r. [$(^2H_6)Me_2SO$]: δ 1.12 (d, 3 H, $J_{5',6'}$ 6.2 Hz, H-6′), 1.94–2.10 (m, 18 H, 6 AcO), 3.51 and 3.54 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 11.4 Hz, H-6a, β and α), 3.65 (m, 1 H, $J_{5,6b}$ 2.6 Hz, H-6b), 3.82 (m, 1 H, $J_{4',5'}$ 9.8 Hz, H-5′), 3.95 and 4.10 (m, 1 H, $J_{4,5}$ 9.9 Hz, H-5, β and α), 4.69 (m, 1 H, $J(\alpha)_{1,2}$ 3.1, $J(\beta)_{1,2}$ 8.9, $J(\alpha)_{2,3}$ 10.2 Hz, H-2), 4.77 (d, 1 H, $J_{1',2}$ 1.3 Hz, H-1′), 4.78 and 5.23 (dd, 1 H, $J(\alpha)_{1,OH}$ 4.9, $J(\beta)_{1,OH}$ 6.5 Hz, H-1, β and α), 4.89 (dd, 1 H, $J_{3',4'}$ 10 Hz, $J_{4',5'}$ 9.8 Hz, H-4′), 4.90 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-4), 5.05 (dd, 1 H, $J_{2',3'}$ 3.5 Hz, H-3′), 5.10 (dd, 1 H, H-2′), 5.23 and 5.37 (dd, 1 H, H-3, β and α), 7.23 and 7.24 (d, 1 H, OH, α and β).

*Geranyl 6-*O*-α-*L*-rhamnopyranosyl-β-*D*-glucopyranoside* (**6**) *and geranyl 2,3,4-tri-*O*-acetyl-6-*O*-α-*L*-rhamnopyranosyl-β-*D*-glucopyranoside* (**7**). — Compound **1** (0.14 mmol) was deacetylated as described for **4**. The crude oily residue was purified by column chromatography (solvent *D*) to give syrupy[8] **6** (0.12 mmol, 85%) and **7** (5.5 μmol, 3%). Compound **6** showed $[\alpha]_D^{21}$ −5.2° (*c* 0.23, ethanol); R_F 0.35 (solvent *D*); ^{1}H-n.m.r., see Tables I and II; f.a.b.m.s.: *m/z* 93 (100), 69 (93), 81 (53), 57 (51), 45 (42), 41 (40), 137 (39), 245 (37), 73 (34), 75 (3), 185 (32), 147 (29), 91 (28), 85 (27), 47 (25), 71 (24), 55 (24), and 43 (20); other significant ions: *m/z* 391 (9), 163 (5.9), 309 (4.1), 153 (3), 554 (2), 325 (1.6), and 299 (0.8); lit.[5] g.l.c.–m.s. of the per(trimethylsilyl) derivative of the natural compound gave fragments at *m/z* 69, 81, 191, 204, and 217. Compound **7** had R_F 0.75 (solvent *D*); ^{1}H-n.m.r., see Tables I and II.

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