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SYNTHESIS OF THE GLYCOALKALOIDS OF *SELAGINELLA DOEDERLEINII* AND STRUCTURE REVISION OF ONE OF THEM[1]

LIN RUI CHAO,[2] ELISABETH SEGUIN, ALEXIOS-LEANDROS SKALTSOUNIS, FRANCOIS TILLEQUIN, and MICHEL KOCH*

Département de Pharmacognosie de l'Université René Descartes, UA au CNRS no. 484, Faculté des Sciences Pharmaceutiques et Biologiques, 4 Avenue de l'Observatoire, F-75006 Paris, France

ABSTRACT.—The syntheses of hordenine-α-L-rhamnopyranoside [**1**] and of the three possible isomers resulting from its glycosylation by (*E*)-6-*O*-cinnamoylglucose, as their acetyl derivatives **3**, **4**, and **5**, have been achieved. These results have led us to revise the structure of the acylated glycoalkaloid previously isolated from *Selaginella doederleinii* from **2** to **6**. In addition, the structure of a minor glycoside isolated from the same plant has been established as **7**, on the basis of the synthesis of its acetyl derivative **14**.

We have recently reported the isolation from *Selaginella doederleinii* Hieron. (Selaginellaceae) of several hordenine-derived glycosides (1). The main constituent belonging to this series is hordenine-α-L-rhamnopyranoside [**1**]. It is accompanied in the plant extract by several minor glycosides of the general structure 6-*O*-cinnamoyl-(or 4-hydroxycinnamoyl-)-glucopyranosyl-rhamnopyranosyl-hordenine. The structure of one of them has been concluded to be (*E*)-hordenine-[6-*O*-cinnamoyl-β-D-glucopyranosyl]-(1↦4)-α-L-rhamnopyranoside [**2**] on the basis of its ^{13}C-nmr data (1), compared with those of flavonoid glycosides with a closely related sugar moiety, previously isolated from *Ginkgo biloba* (2,3). Nevertheless, more recently, an alternative structure with a different position of linkage between glucose and rhamnose units has been postulated for these flavonoids, on the basis of similar ^{13}C-nmr data (4). Finally, the correct structures of *Ginkgo* flavonoids were unequivocally established, using ^{1}H-nmr multiple-pulse experiments (5). It was therefore obvious that ^{13}C nmr did not permit us to assign unambiguously the site of glucosylation, at C-2, C-3, or C-4 on the rhamnose unit, in such derivatives (6).

We report here the synthesis of hordenine-α-L-rhamnopyranoside [**1**] and of the three possible isomers resulting from its glycosylation by (*E*)-6-*O*-cinnamoyl glucose, as their acetyl derivatives **3**, **4**, and **5**. These results permitted us to determine with certainty the structure of the acylated glycoside previously isolated from *S. doederleinii*, which should be revised from **2** to **6**. In addition, the same syntheses using 4-hydroxycinnamic acid as acylating unit allowed us to depict as **7** the structure of a minor glycoalkaloid isolated initially in too small an amount to record its ^{13}C-nmr spectrum.

RESULTS AND DISCUSSION

To our knowledge, glycosidation reactions targeted towards the synthesis of *O*-α-L-rhamnosides of phenols have not been systematically explored. Therefore, it was logical to try to synthesize **1** by various reactions previously described either for the rhamnosidation of alcohols or for the glycosidation of phenols by various carbohydrate units.

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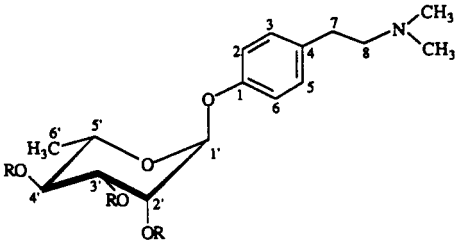
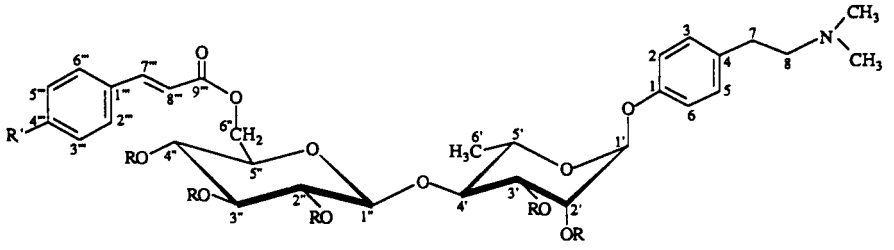
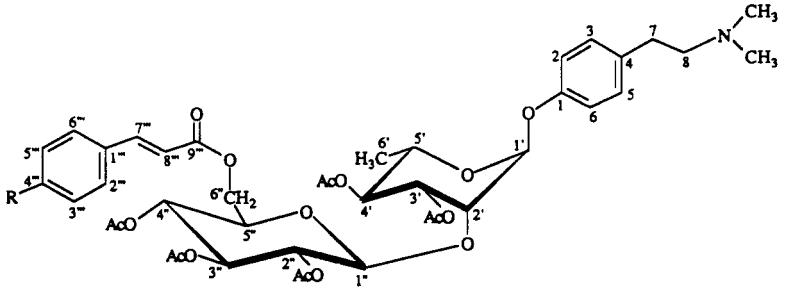
[2]On leave from Beijing College of Traditional Chinese Medicine, He Ping Jie Bei Kou, Beijing, China.



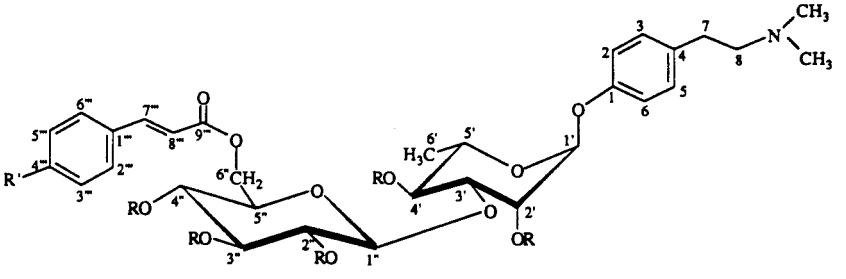
1 R=H **11** R=Ac



2 R=R′=H **5** R=Ac, R′=H **15** R=Ac, R′=OAc



3 R=H **13** R=OAc

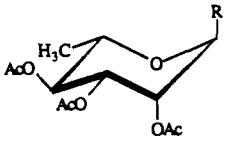


4 R=Ac, R′=H **6** R=R′=H **7** R=H, R′=OH **14** R=Ac, R′=OAc

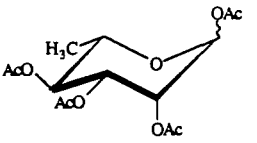
These reactions involve 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide [**8**], 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranose [**9**] or 1,2,3,4-tetra-*O*-acetyl-α,β-L-rhamnopyranose [**10**] (7).

The attempts to condense hordenine with **8** using either Königs-Knorr derived conditions (8–10) or phase-transfer catalysis (11,12) did not afford the expected compound **11** but rather the corresponding orthoester **12** (13–16) in 20–65% yield. Condensation of **9** with hordenine, carried out either with silver trifluoromethanesulfonate (17) or with triphenylphosphine and diethyl azodicarboxylate (18), led to an

equimolecular mixture of the orthoester **12** and the expected protected glycoside **11** in 20% overall yield. Finally, hordenine-(2,3,4-tri-*O*-acetyl)-*O*-α-L-rhamnopyranoside [**11**] could be readily obtained in 46% yield by treatment of a solution of hordenine and 1,2,3,4-tetra-*O*-acetyl-α,β-L-rhamnopyranose [**10**] in MeCN with tin tetrachloride (19–23). Deprotection of **11** by NaOMe in MeOH (24) smoothly afforded hordenine-α-L-rhamnopyranoside [**1**], identical with the natural product, in almost quantitative yield.



8 R=Br **9** R=OH



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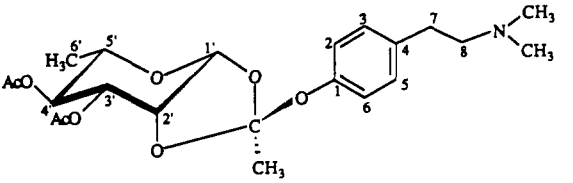

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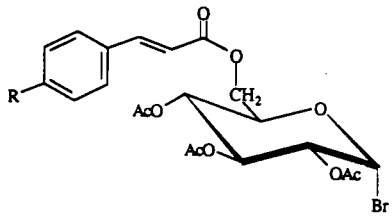
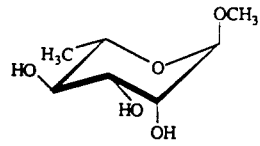
The synthesis of the acylated alkaloid-glycosides **3**, **4**, and **5** and of their acetoxycinnamoyl counterparts **13**, **14**, and **15** involved successively (a) the synthesis of the acylated bromoglucose units **16** and **17**, (b) the coupling of these bromo-derivatives with the unprotected rhamnose unit **18** in order to obtain simultaneously the three possible isomers, linked 1↦2, 1↦3, and 1↦4, and (c) the condensation of each disaccharide unit with hordenine by the method previously used for the synthesis of **11**.

Condensation of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose [**19**] with either (*E*)-cinnamoyl chloride [**20**] or (*E*)-4-acetoxycinnamoyl chloride [**21**] (25) in pyridine containing catalytic amounts of 4-(*N*,*N*-dimethylamino)-pyridine led to (*E*)-1,2,3,4-tetra-*O*-acetyl-6-*O*-cinnamoyl-β-D-glucopyranose [**22**] and (*E*)-6-*O*-(4-acetoxycinnamoyl)-1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose [**23**]. Conversion of **22** and **23** into the corresponding bromides **16** and **17** was achieved by treatment with HBr in anhydrous HOAc.

Reaction of methyl-α-L-rhamnopyranoside [**18**] with either **16** or **17** (26) in the presence of mercuric cyanide (10) furnished a mixture of **24/25/26** or **27/28/29** in 62–65% overall yield. These compounds were difficult to separate from each other on a preparative scale. Therefore, only a small sample of the major compound **28** has been prepared from the former mixture for analytical purposes. The unseparable mixtures of **24/25/26** and **27/28/29** were then directly submitted to acetolysis (10), which afforded the acylated disaccharides **30/31/32** and **33/34/35**. These compounds could be easily separated by repeated cc. Each of them has been characterized by its ^{1}H-nmr spectrum, and full assignments of the signals have been deduced from 2D COSY 45° experiments (27–29). The abnormally high shielding of the signals of H-2 in **30** and **33**, H-3 in **31** and **34**, and H-4 in **32** and **35** indicates that these positions are not acetylated and therefore correspond to the position of linkage of the glucose moiety on the rhamnose unit (30–32). The assignments of the signals of the ^{13}C-nmr spectra of compounds **30–35** (Table 1) have then been deduced from 2D ^{1}H-^{13}C heteronuclear shift correlation



16 R=H
17 R=OAc



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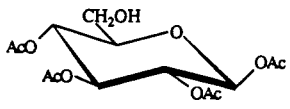

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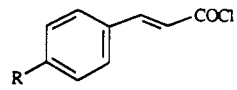


20 R=H
21 R=OAc

TABLE 1. ^{13}C-nmr Spectra of Compounds **30**, **33**, **31**, **34**, **32** and **35** (75 MHz, $CDCl_3$, TMS, δ ppm).

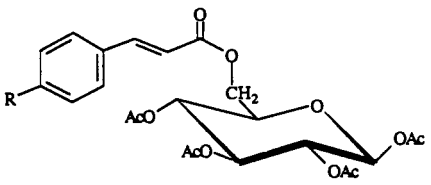
Carbon	Compound					
	30	**33**	**31**	**34**	**32**	**35**
C-1	92.2	92.5	90.1	90.4	90.4	90.4
C-2	75.6	76.0	70.0	70.2	68.8	68.8
C-3	70.4	70.7	73.8	74.1	70.6	70.7
C-4	70.4	70.7	71.6	71.9	76.2	76.3
C-5	68.3	68.6	68.0	68.4	69.0	69.0
C-6	17.1	17.5	17.0	17.3	17.5	17.6
C-1′	101.8	102.1	100.5	100.7	100.5	100.5
C-2′	70.8	71.1	70.8	71.1	71.1	71.1
C-3′	72.1	72.4	72.3	72.6	72.7	72.7
C-4′	68.6	68.8	68.1	68.4	68.8	68.8
C-5′	71.7	72.0	71.5	71.7	71.4	71.4
C-6′	61.8	62.1	61.6	61.8	62.0	62.0
C-1″	134.1	132.1	133.8	131.6	133.9	131.6
C-2″	128.0	122.1	127.8	122.1	128.0	122.1
C-3″	128.5	129.4	128.6	129.3	128.8	129.2
C-4″	130.1	152.2	130.2	152.0	130.4	152.2
C-5″	128.5	129.4	128.6	129.3	128.8	129.2
C-6″	128.0	122.1	127.8	122.1	128.0	122.1
C-7″	145.2	144.4	145.4	144.6	145.6	144.6
C-8″	117.2	117.6	116.9	117.2	116.9	117.1
C-9″	166.1	166.4	166.0	166.0	166.1	166.0
OCOMe	170.0	170.4	169.8	170.2	170.0	170.1
	169.9	170.3	169.5	169.6	169.3	168.9
	169.1	169.5	169.1	169.4	169.5 2C	169.6 2C
	168.0	169.4	168.9	169.0	169.2	169.3 2C
	169.0 2C	169.3	168.7	169.2 2C	168.3	
		169.2	167.8			
$OCOCH_3$	20.5 2C	21.2	20.5	21.0	20.7	20.9
	20.4	20.8	20.2	20.8	20.5	20.8
	20.2	20.9 2C	20.4 2C	20.7 2C	20.4 2C	20.6 2C
	20.3 2C	20.7 2C	20.1	20.5 2C	20.3	20.4 2C
			20.0		20.2	
OCOMe-4″		168.4		168.1		168.4
$OCOCH_3$-4″		20.6		20.3		20.2

experiments (27–29). In terms of regioselectivity, it should be noted that the yields of glycosides followed the order 1↦3>1↦4>1↦2, as previously reported for the condensation of benzyl-α-L-rhamnopyranoside with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (26).

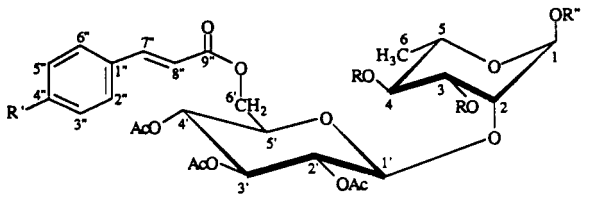
Finally, reaction of the acylated disaccharides **30–35** with hordenine in the presence of tin tetrachloride in MeCN (19–23), gave the corresponding glycosides **3**, **4**, **5**, **13**, **14**, and **15** in 50–60% yield.

The peracetyl derivative of the acylated alkaloid glycoside isolated from *S. doederleinii* (1) is identical in all respects with **4** and differs from both **5** and **3**. The structure of the natural alkloid should be revised from **2** to **6**. In addition, compound **14** is identical with the acetyl derivative of a minor glycoalkaloid isolated from *S. doederleinii*, whose structure is therefore established as **7**.

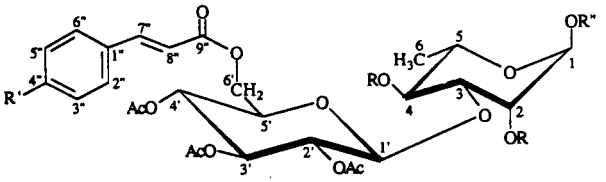
Full interpretation of the ^{1}H-nmr spectra of acetylglycosides **3–5** and **13–15** has been deduced from 2D COSY spectra. The assignments of the ^{13}C-nmr signals have been deduced from heteronuclear shift correlation experiments (Table 2) (27–29). A study of the ^{13}C-^{1}H long-range couplings observed in the COLOC spectrum of **4** (29,33) allowed us to assign unambiguously most of the quaternary ^{13}C resonances. Furthermore, this experiment provides a direct evidence for the sequence of the different units by the observation of long-range correlations between C-1 and H-1′, H-3′ and C-1″, and CH_2-6″ and C-9‴.



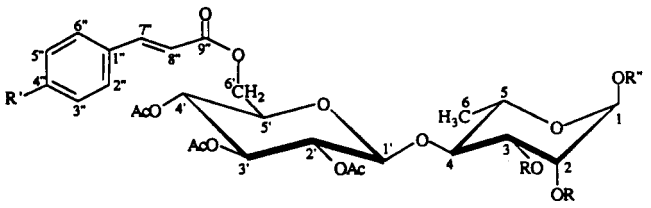
22 R=H
23 R=OAc



24 R=R′=H, R″=Me
27 R=H, R′=OAc, R″=Me
30 R=R″=Ac, R′=H
33 R=R″=Ac, R′=OAc



25 R=R′=H, R″=Me
28 R=H, R′=OAc, R″=Me
31 R=R″=Ac, R′=H
34 R=R″=Ac, R′=OAc



26 R=R′=H, R″=Me
29 R=H, R′=OAc, R″=Me
32 R=R″=Ac, R′=H
35 R=R″=Ac, R′=OAc

TABLE 2. ^{13}C-nmr Spectra of Compounds **3**, **13**, **4**, **14**, **5** and **15** (75 MHz, $CDCl_3$, TMS, δ ppm).

Carbon	Compound					
	3	**13**	**4**	**14**	**5**	**15**
C-1	154.5	154.6	154.2	154.6	154.4	154.9
C-2	116.4	116.2	116.3	115.5	116.6	117.1
C-3	129.8	130.1	129.4	130.3	129.6	130.1
C-4	134.1	132.2	133.9	132.3	134.5	132.1
C-5	129.8	130.1	129.4	130.3	129.6	130.1
C-6	116.4	116.2	116.3	115.5	116.6	117.1
C-7	31.9	31.9	31.7	31.8	33.2	31.9
C-8	60.5	60.2	60.2	60.1	61.4	60.1
NMe_2	44.3	44.4	44.2	44.1	45.2	44.6
C-1′	96.7	96.9	95.4	95.6	95.8	95.9
C-2′	76.5	76.7	71.2	70.5	69.0	67.7
C-3′	71.1	71.2	74.4	74.3	71.0	71.4
C-4′	71.0	71.0	72.0	72.2	76.8	77.4
C-5′	66.9	67.0	66.7	66.7	70.1	70.3
C-6′	17.1	17.5	17.1	17.5	17.7	17.9
C-1″	102.1	102.3	102.8	101.0	100.7	101.0
C-2″	71.2	71.3	71.0	71.0	71.1	71.5
C-3″	72.3	72.5	72.5	72.3	73.0	73.1
C-4″	68.7	68.8	68.4	68.4	67.5	69.2
C-5″	72.1	72.2	71.6	71.5	71.2	71.8
C-6″	62.1	62.3	62.1	62.4	62.2	62.3
C-1‴	132.2	131.9	132.4	131.6	132.1	131.7
C-2‴	128.3	129.6	128.0	129.6	128.3	129.7
C-3‴	128.9	122.3	128.6	121.9	129.0	122.6
C-4‴	130.5	152.3	130.1	152.2	130.6	152.6
C-5‴	128.9	122.3	128.6	121.9	129.0	122.6
C-6‴	128.3	129.6	128.0	129.6	128.3	129.7
C-7‴	145.7	144.6	145.5	143.5	145.9	144.9
C-8‴	117.1	117.3	116.9	116.5	117.1	118.2
C-9‴	166.4	166.1	166.2	165.9	166.4	166.5
OCOMe	170.4	170.5 2C	170.0 2C	170.1 2C	170.4	170.5
	170.3	170.3	169.4	169.1 2C	170.0	170.3
	169.7	169.5	169.1	168.9	169.7	169.9
	169.5	169.2	168.9		169.5	169.7
	169.4				169.4	169.5
$OCOCH_3$	20.9	21.4 2C	20.6 2C	21.6	21.0	21.4
	20.8 2C	20.9 2C	20.3 2C	20.9 2C	20.9	21.2 2C
	20.7 2C	20.7	20.2	20.6 2C	20.6 2C	20.9 2C
					20.5	
OCOMe-4‴		168.6		168.6		168.4
$OCOCH_3$-4‴		20.6		20.5		20.6

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Spectra were recorded on the following apparatus: uv, Unicam SP 800; ir, Beckman 4250 or Pye-Unicam SP 3-200; ms, Nermag R 10-10C; nmr Bruker HX 270 or AC 300. Multi-impulsional experiments were performed using the standard Bruker microprograms.

O-exo-3,4-DI-*O*-ACETYL-1,2-*O*-[4-(2-DIMETHYLAMINO-1-ETHYL)-1-PHENOXY]-ETHYLIDENE-α-L-RHAMNOPYRANOSE [**12**].—Mercuric cynanide (370 mg, 1.46 mmol) and hordenine (130 mg, 0.8 mmol) were added under stirring to a solution of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide [**8**] (340 mg, 1 mmol) in anhydrous MeCN (5 ml). The reaction mixture was stirred at 20° for 12 h. The MeCN was removed by evaporation under reduced pressure, and the remaining syrup was dissolved in

$CHCl_3$ (50 ml). The $CHCl_3$ solution was washed with 10% aqueous KBr (2 × 40 ml), saturated aqueous $NaHCO_3$ (40 ml), and H_2O (2 × 40 ml). The $CHCl_3$ was evaporated, and the remaining syrup yielded **12** after purification by flash chromatography [silica, CH_2Cl_2-MeOH-concentrated NH_3 (90:10:1)]: yield 225 mg (65%); $[\alpha]^{20}D$ −5° ($CHCl_3$, c = 1); uv λ MeOH max nm (log ε) 243 (2.91), 266 (2.77), 273 (2.78); ir (KBr) ν max cm^{-1} 2950, 1650, 1505, 1390, 1380, 1225, 1170, 1060; ms (dci NH_3) *m/z* (%) $[M+H]^+$ 438 (100), 273 (14), 166 (54); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.12 (2H, d, J = 9 Hz, H-3, H-5), 7.04 (2H, d, J = 9 Hz, H-2, H-6), 5.32 (1H, d, J = 2.5 Hz, H-1′), 5.05 (1H, t, J = 9 Hz, H-4′), 5.00 (1H, dd, J = 9 Hz, J' = 3.5 Hz, H-3′), 4.15 (1H, dd, J = 3.5 Hz, J' = 2.5 Hz, H-2′), 3.47 (1H, dq, J = 9 Hz, J' = 7 Hz, H-5′), 2.91 (2H, m, H_2-7), 2.83 (2H, m, H_2-8), 2.55 (6H, s, NMe_2), 2.12, 2.05 (2 × 3H, 2s, 3′-OAc, 4′-OAc), 1.82 (3H, s, CMe), 1.22 (3H, d, J = 7 Hz, Me-6′).

HORDENINE-(2,3,4-TRI-*O*-ACETYL)-α-L-RHAMNOPYRANOSIDE [**11**].—Stannic chloride (0.3 ml) was added to a solution of 1,2,3,4-tetra-*O*-acetyl-α,β-L-rhamnopyranose [**10**] (825 mg, 2.5 mmol) and hordenine (165 mg, 1 mmol) in dry MeCN (10 ml), and the mixture was stirred at 20° for 24 h. The solution was diluted with H_2O (20 ml), alkalinized with saturated aqueous NH_3 (5 ml), filtered, and extracted by CH_2Cl_2 (3 × 30 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated, and the residue yielded **11** after purification by flash chromatography [silica, CH_2Cl_2-MeOH-concentrated NH_3 (90:10:1)]: yield 201 mg (46%); $[\alpha]^{20}D$ −2° ($CHCl_3$, c = 0.5); ir (KBr) ν max cm^{-1} 2995, 2950, 1750, 1610, 1510, 1390, 1375, 1240, 1225, 1175, 1055, 955, 900; ms (dci NH_3) *m/z* (%) $[M+H]^+$ 438 (100), 166 (30); ^1H-nmr data identical with those previously published (1).

HORDENINE-α-L-RHAMNOPYRANOSIDE [**1**].—To a solution of **11** (90 mg, 0.2 mmol) in CH_2Cl_2 (10 ml), 1 N NaOMe in MeOH (0.2 ml) was added, and the mixture was stirred at 20° for 3 h. After neutralization by addition of Amberlite IR 50 H^+ ion exchange resin and filtration, the solvents were removed by evaporation to afford pure **1**, identical with the natural product isolated from *S. doederleinii* ($[\alpha]^{20}D$, uv, ir, ms, ^1H nmr, tlc), yield 25 mg (40%).

(*E*)-1,2,3,4-TETRA-*O*-ACETYL-6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSE [**22**].—To an ice-cooled solution of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose [**19**] (6 g, 17.2 mmol) and (*E*)-cinnamoyl chloride [**20**] (16.6 g, 100 mmol) in dry pyridine (200 ml), was added 4-(*N,N*-dimethylamino)pyridine (DMAP) (3 g). The reaction mixture was stirred at 20° for 5 days and poured on cold H_2O (5 liters). After 24 h, the precipitate was filtered and purified by flash chromatography [silica, hexanes-EtOAc (90:10, 70:30, 50:50)] to give **22**: yield 6.75 g (82%); $[\alpha]^{20}D$ +20° ($CHCl_3$, c = 1); uv ($CHCl_3$) λ max nm (log ε) 282 (4.57); ms (dci NH_3) *m/z* (%) $[M+NH_4]^+$ 496 (100), 419 (90), 131 (95); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.74 (1H, d, J = 16 Hz, H-7′), 7.58 (2H, m, H-2′, H-6′), 7.42 (3H, m, H-3′, H-4′, H-5′), 6.49 (1H, d, J = 16 Hz, H-8′), 5.78 (1H, d, J = 9 Hz, H-1), 5.23–5.17 (3H, m, H-2, H-3, H-4), 4.34 (2H, m, H-6a, H-6b), 3.94 (1H, ddd, J = 10 Hz, J' = 6 Hz, J'' = 3 Hz, H-5), 2.13, 2.05, 2.04, 2.02 (4 × 3H, 4s, 4 × OAc).

(*E*)-6-*O*-(4-ACETOXYCINNAMOYL)-1,2,3,4-TETRA-*O*-ACETYL-β-D-GLUCOPYRANOSE [**23**].—In a procedure similar to the one used for the preparation of **22**, **23** was obtained from **19** (6 g, 17.2 mmol) and (*E*)-4-acetoxycinnamoyl chloride [**21**] (20.8 g, 100 mmol): yield 8.02 g (87%); $[\alpha]^{20}D$ +24° ($CHCl_3$, c = 1); uv ($CHCl_3$) λ max nm (log ε) 285 (4.74); ms (dci NH_3) *m/z* (%) $[M+NH_4]^+$ 554 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.64 (1H, d, J = 16 Hz, H-7′), 7.52 (2H, d, J = 9 Hz, H-2′, H-6′), 7.09 (2H, d, J = 9 Hz, H-3′, H-5′), 6.38 (1H, d, J = 16 Hz, H-8′), 5.70 (1H, d, J = 8 Hz, H-1), 5.28–5.11 (3H, m, H-2, H-3, H-4), 4.29 (2H, m, H-6a, H-6b), 3.89 (1H, ddd, J = 10 Hz, J' = 6 Hz, J'' = 3 Hz, H-5), 2.27 (3H, s, ArOAc), 2.08, 2.00, 1.99, 1.96 (4 × 3H, 4s, 4 × OAc).

(*E*)-2,3,4-TRI-*O*-ACETYL-6-*O*-CINNAMOYL-α-D-GLUCOPYRANOSYL BROMIDE [**16**].—HBr in HOAc (40% solution, 8 ml) was added dropwise under stirring at 0° to a solution of **22** (1.43 g, 0.3 mmol) in dry CH_2Cl_2 (10 ml). After stirring 5 min at 0° and 15 min at 20°, the reaction mixture was poured on ice-cold H_2O (75 ml), and the resulting two-phase system was vigorously stirred for 15 min. CH_2Cl_2 (10 ml) was added and the organic layer was separated, washed with saturated aqueous $NaHCO_3$ (20 ml), H_2O (3 × 20 ml), dried over anhydrous Na_2SO_4 and evaporated to afford **16**: yield 1.03 g (68%); $[\alpha]^{20}D$ +26° (MeOH, c = 1); uv (MeOH) λ max nm (log ε) 278 (4.44), ms (dic NH_3) *m/z* (%) $[M+NH_4]^+$ 518 (60), $[M+NH_4]^+$ 516 (59), 454 (60), 412 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.73 (1H, d, J = 16 Hz, H-7′), 7.54 (2H, m, H-2′, H-6′), 7.41 (3H, m, H-3′, H-4′, H-5′), 6.64 (1H, d, J = 3 Hz, H-1), 6.48 (1H, d, J = 16 Hz, H-8′), 5.60 (1H, t, J = 9 Hz, H-3), 5.29 (1H, t, J = 9 Hz, H-4), 4.88 (1H, dd, J = 9 Hz, J' = 3 Hz, H-2), 4.38 (3H, m, H-5, H-6a, H-6b), 2.09, 2.07, 2.02 (3 × 3H, 3s, 3 × OAc).

(*E*)-6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-α-D-GLUCOPYRANOSYL BROMIDE [**17**].—The acyl derivative **23** (1.78 g, 0.3 mmol) was converted to compound **17** following the procedure described above for the preparation of **16** from **22**: yield 1.54 g (92%); $[\alpha]^{20}D$ +23° (MeOH, c = 1); ms (dci NH_3) $[M+NH_4]^+$ 576 (82), $[M+NH_4]^+$ 574 (81), 189 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm

7.69 (1H, d, J = 16 Hz, H-7'), 7.55 (2H, d, J = 9 Hz, H-2', H-6'), 7.11 (2H, d, J = 9 Hz, H-3', H-5'), 6.62 (1H, d, J = 4 Hz, H-1), 6.41 (1H, d, J = 16 Hz, H-8'), 5.59 (1H, t, J = 9 Hz, H-3), 5.21 (1H, t, J = 9 Hz, H-4), 4.87 (1H, dd, J = 9 Hz, J' = 4 Hz, H-2), 4.37 (3H, m, H-5, H-6a, H-6b), 2.31 (3H, s, ArOAc), 2.10, 2.07, 2.04 (3 × 3H, 3s, 3 × OAc).

REACTION OF **16** WITH METHYL-α-L-RHAMNOPYRANOSIDE [**18**].—To a solution of methyl-α-L-rhamnopyranoside [**18**] (1.25 g, 7 mmol) and anhydrous mercuric cyanide (2.7 g) in dry MeCN (30 ml) was added the bromide **16** (5.70 g, 11.5 mmol) with stirring; the stirring was continued for 5 h at 20°. The MeCN was removed from the reaction mixture under reduced pressure, and the remaining syrup was dissolved in CH_2Cl_2 (50 ml). The CH_2Cl_2 was washed with 1 N aqueous KBr (2 × 25 ml) and H_2O (25 ml) and dried over anhydrous Na_2SO_4. The solvent was removed, and the remaining syrup was submitted to flash chromatography [silica, hexanes-EtOAc (25:75)] to give an unseparable mixture of **24**, **25**, and **26**; overall yield 2.59 g (62%).

REACTION OF **17** WITH METHYL-α-L-RHAMNOPYRANOSIDE [**18**].—In a procedure similar to the one used for the condensation of **16** with **18**, the bromide **17** (6.40 g, 11.5 mmol) was reacted with **18** (1.25 g, 7 mmol) to afford a mixture of **27**, **28**, and **29**; overall yield 2.97 g (65%).

(*E*)-METHYL-[6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSYL]-(1→3)-α-L-RHAMNOPYRANOSIDE [**28**].—Repeated cc [silica H, hexanes-EtOAc (40:60)] of the mixture of **27**, **28**, and **29** permitted us to prepare an analytical sample of the major component **28**: $[\alpha]^{20}D$ +3° ($CHCl_3$, c = 1); uv ($CHCl_3$) λ max nm (log ε) 287 (4.62); ir (KBr) ν max cm^{-1} 3520, 2940, 2840, 1760, 1635, 1605, 1510, 1380, 1320, 1170, 1050, 980, 910, 840; ms (dci NH_3) m/z (%) $[M + NH_4]^+$ 672 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.67 (1H, d, J = 16 Hz, H-7''), 7.53 (2H, d, J = 8.5 Hz, H-2'', H-6''), 7.10 (2H, d, J = 8.5 Hz, H-3'', H-5''), 6.38 (1H, d, J = 16 Hz, H-8''), 5.22 (1H, t, J = 9 Hz, H-3'), 5.08 (2H, m, H-2', H-4'), 4.67 (1H, d, J = 8 Hz, H-1'), 4.57 (1H, d, J = 2 Hz, H-1), 4.40 (1H, dd, J = 12 Hz, J' = 2 Hz, H-6'b), 4.29 (1H, dd, J = 12 Hz, J' = 6 Hz, H-6'a), 3.98 (1H, t, J = 2 Hz, H-2), 3.84 (1H, m, H-5'), 3.66 (3H, m, H-3, H-4, H-5), 3.21 (3H, s, OMe), 2.84, 2.56 (2 × 1H, 2 br s, D_2O exchangeable, 2-OH, 4-OH), 2.30 (3H, s, ArOAc), 2.02, 2.01, 1.98 (3 × 3H, 3s, 3 × OAc), 1.27 (3H, d, J = 6 Hz, Me-6).

ACETOLYSIS OF **24**, **25**, AND **26**.—The mixture of compounds **24**, **25**, and **26** prepared above (4.18 g) in Ac_2O (17 ml) was shaken with 2% concentrated H_2SO_4 in Ac_2O (34 ml) at 20° for 4 h. The reaction mixture was diluted with CH_2Cl_2 (300 ml) and washed with H_2O (2 × 300 ml), saturated aqueous $NaHCO_3$ (2 × 300 ml), and again with H_2O (2 × 300 ml). The CH_2Cl_2 solution was dried over anhydrous Na_2SO_4 and evaporated. Separation by cc [silica H, hexanes-EtOAc (70:30, 60:40, 50:50)] of the recovered syrup gave **30** (235 mg, 4.7%), **31** (825 mg, 13.5%), and **32** (383 mg 7.7%).

(*E*)-(2,3,4-TRI-*O*-ACETYL-6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSYL)-(1→2)-1,3,4-TRI-*O*-ACETYL-α-L-RHAMNOPYRANOSE [**30**].—Colorless foam: $[\alpha]^{20}D$ −22° ($CHCl_3$, c = 1); $C_{33}H_{40}O_{17}$; found C 55.70, H 5.79, O 38.31, calcd C 55.93, H 5.69, O 38.40; uv ($CHCl_3$) λ max nm (log ε) 282 (4.72); ir (KBr) ν max cm^{-1} 3000, 2950, 1760, 1640, 1455, 1375, 1220, 1170, 1045, 965, 780; ms (dci NH_3) m/z (%) $[M + NH_4]^+$ 726 (93), 131 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.70 (1H, d, J = 16 Hz, H-7''), 7.62 (2H, m, H-2'', H-6''), 7.38 (3H, m, H-3'', H-4'', H-5''), 6.49 (1H, d, J = 16 Hz, H-8''), 6.16 (1H, d, J = 1.5 Hz, H-1), 5.24 (1H, t, J = 9 Hz, H-3'), 5.16 (1H, dd, J = 9 Hz, J' = 3 Hz, H-3), 5.10 (2H, m, H-2', H-4'), 5.00 (1H, t, J = 9 Hz, H-4), 4.58 (1H, d, J = 8 Hz, H-1'), 4.32 (2H, m, H-6'a, H-6'b), 4.04 (1H, dd, J = 3 Hz, J' = 1.5 Hz, H-2), 3.89 (1H, m, H-5), 3.79 (1H, m, H-5'), 2.13, 2.08, 2.04, 2.03, 2.03, 2.02, (6 × 3H, 6s, 6 × OAc), 1.21 (3H, d, J = 6 Hz, Me-6); ^{13}C nmr see Table 1.

(*E*)-(2,3,4-TRI-*O*-ACETYL-6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSYL)-(1→3)-1,2,4-TRI-*O*-ACETYL-α-L-RHAMNOPYRANOSE [**31**].—Colorless foam: $[\alpha]^{20}D$ −12° ($CHCl_3$, c = 1); $C_{33}H_{40}O_{17}$; found C 55.76, H 5.66, O 38.33, calcd C 55.93, H 5.69, O 38.40; uv ($CHCl_3$) λ max nm (log ε) 284 (4.70); ir KBr ν max cm^{-1} 3000, 2950, 1760, 1640, 1455, 1375, 1220, 1170, 1065, 1040, 975, 910, 775; ms (dci NH_3) $[M + NH_4]^+$ 726 (100), 131 (55); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.73 (1H, d, J = 16 Hz, H-7''), 7.53 (2H, m, H-2'', H-6''), 7.37 (3H, m, H-3'', H-4'', H-5''), 6.44 (1H, d, J = 16 Hz, H-8''), 5.98 (1H, d, J = 1.5 Hz, H-1), 5.19 (1H, dd, J = 3 Hz, J' = 1.5 Hz, H-2), 5.17 (1H, t, J = 9 Hz, H-3'), 5.12 (1H, t, J = 9 Hz, H-4'), 5.09 (1H, t, J = 9 Hz, H-4), 4.97 (1H, t, J = 9 Hz, H-2'), 4.69 (1H, d, J = 9 Hz, H-1'), 4.31 (2H, m, H-6'a, H-6'b), 4.11 (1H, dd, J = 9 Hz, J' = 3 Hz, H-3), 3.80 (2H, m, H-5, H-5'), 2.12, 2.11, 2.03, 2.03, 1.99, 1.98 (6 × 3H, 6s, 6 × OAc), 1.20 (3H, d, J = 6 Hz, Me-6); ^{13}C nmr see Table 1.

(*E*)-(2,3,4-TRI-*O*-ACETYL-6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSYL)-(1→4)-1,2,3-TRI-*O*-ACETYL-α-L-RHAMNOPYRANOSE [**32**].—Colorless foam: $[\alpha]^{20}D$ −46° ($CHCl_3$, c = 1); $C_{33}H_{40}O_{17}$; found C

55.78, H 5.80, O 38.45, calcd C 55.93, H 5.69, O 38.40; uv $CHCl_3$ λ max nm (log ε) 281 (4.65); ir (KBr) ν max cm^{-1} 2995, 1945, 1760, 1640, 1455, 1375, 1250, 1225, 1170, 1065, 1040, 980, 910, 780; ms (dci NH_3) *m/z* (%) $[M+NH_4]^+$ 726 (100), 131 (20); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.71 (1H, d, $J=17$ Hz, H-7″), 7.54 (2H, m, H-2″, H-6″), 7.38 (3H, m, H-3″, H-4″, H-5″), 6.43 (1H, d, $J=17$ Hz, H-8″), 5.94 (1H, d, $J=1.5$ Hz, H-1), 5.23 (1H, dd, $J=10$ Hz, $J'=3$ Hz, H-3), 5.18 (1H, t, $J=9$ Hz, H-3′), 5.13 (1H, dd, $J=3$ Hz, $J'=1.5$ Hz, H-2), 5.09 (1H, t, $J=9$ Hz, H-4′), 4.97 (1H, t, $J=9$ Hz, H-2′), 4.70 (1H, d, $J=9$ Hz, H-1′), 4.46 (1H, dd, $J=12$ Hz, $J'=3$ Hz, H-6′b), 4.26 (1H, dd, $J=12$ Hz, $J'=6$ Hz, H-6′a), 3.83 (2H, m, H-5, H-5′), 3.68 (1H, t, $J=10$ Hz, H-4), 2.12, 2.08, 2.03, 2.02, 1.98, 1.97 (6 × 3H, 6s, 6 × OAc), 1.33 (3H, d, $J=6$ Hz, Me-6); ^{13}C nmr see Table 1.

ACETOLYSIS OF **27**, **28**, AND **29**.—The mixture of compounds **27**, **28**, and **29** (2.50 g) was submitted to acetolysis in a procedure similar to that described for **24**, **25**, and **26** and gave **33** (61.5 mg, 2.1%), **34** (381 mg, 13%), and **35** (135 mg, 4.6%).

(*E*)-[6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSYL]-(1↦2)-1,3,4-TRI-*O*-ACETYL-α-L-RHAMNOPYRANOSE [**33**].—Colorless foam: $[\alpha]^{20}D$ −27° ($CHCl_3$, $c=0.5$); $C_{35}H_{42}O_{19}$; found C 54.68, H 5.70, O 39.78, calcd C 54.83, H 5.52, O 39.65; uv ($CHCl_3$) λ max nm (log ε) 284 (4.62); ir (KBr) ν max cm^{-1} 2920, 1755, 1635, 1600, 1510, 1435, 1375, 1225, 1170, 1050, 960, 910, 840; ms (dci NH_3) *m/z* (%) $[M+NH_4]^+$ 784 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.70 (1H, d, $J=16$ Hz, H-7″), 7.60 (2H, d, $J=9$ Hz, H-2″, H-6″), 7.13 (2H, d, $J=9$ Hz, H-3″, H-5″), 6.47 (1H, d, $J=16$ Hz, H-8″), 6.17 (1H, d, $J=1.5$ Hz, H-1), 5.24 (1H, t, $J=9$ Hz, H-3′), 5.16 (1H, dd, $J=9$ Hz, $J'=3$ Hz, H-3), 5.08 (2H, *m*, H-2′, H-4′), 5.00 (1H, t, $J=9$ Hz, H-4), 4.57 (1H, d, $J=8$ Hz, H-1′), 4.32 (2H, m, H-6′a, H-6′b), 4.04 (1H, dd, $J=3$ Hz, $J'=1.5$ Hz, H-2), 3.91 (1H, m, H-5), 3.78 (1H, m, H-5′), 2.32 (3H, s, ArOAc), 2.13, 2.08, 2.06, 2.05, 2.05, 2.04 (6 × 3H, 6s, 6 × OAc), 1.21 (3H, d, $J=6$ Hz, Me-6); ^{13}C nmr see Table 1.

(*E*)-[6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSYL]-(1↦3)-1,2,4-TRI-*O*-ACETYL-α-L-RHAMNOPYRANOSE [**34**].—Colorless foam: $[\alpha]^{20}D$ −3.5° ($CHCl_3$, $c=1$); $C_{35}H_{42}O_{19}$; found C 54.69, H 5.72, O 39.49, calcd C 54.83, H 5.52, O 39.65; uv ($CHCl_3$) λ max nm (log ε) 285 (4.60); ir (KBr) ν max cm^{-1} 3000, 2950, 1760, 1640, 1605, 1510, 1435, 1375, 1225, 1170, 1060, 975, 910, 840; ms (dci NH_3) *m/z* (%) $[M+NH_4]^+$ 784 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.71 (1H, d, $J=16$ Hz, H-7″), 7.56 (2H, d, $J=9$ Hz, H-2″, H-6″), 7.12 (2H, d, $J=9$ Hz, H-3″, H-5″), 6.41 (1H, d, $J=16$ Hz, H-8″), 5.98 (1H, d, $J=1.5$ Hz, H-1), 5.19 (1H, dd, $J=3$ Hz, $J'=1.5$ Hz, H-2), 5.13 (1H, t, $J=9$ Hz, H-3′), 5.09 (2H, 2t, $J=9$ Hz, H-4, H-4′), 4.95 (1H, t, $J=9$ Hz, H-2′), 4.68 (1H, d, $J=9$ Hz, H-1′), 4.31 (2H, m, H-6′a, H-6′b), 4.10 (1H, dd, $J=9$ Hz, $J'=3$ Hz, H-3), 3.80 (2H, m, H-5, H-5′), 2.31 (3H, s, ArOAc), 2.09, 2.08, 2.03, 2.01, 2.00, 1.97 (6 × 3H, 6s, 6 × OAc), 1.18 (3H, d, $J=6$ Hz, Me-6); ^{13}C nmr see Table 1.

(*E*)-[6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSYL]-(1↦4)-1,2,3-TRI-*O*-ACETYL-α-L-RHAMNOPYRANOSE [**35**].—Colorless foam: $[\alpha]^{20}D$ −39° ($CHCl_3$, $c=1$); $C_{35}H_{42}O_{19}$; found C 54.74, H 5.75, O 39.65, calcd C 54.83, H 5.52, O 39.65; uv ($CHCl_3$) λ max nm (log ε) 286 (4.64); ir (KBr) ν max cm^{-1} 2950, 1760, 1635, 1605, 1510, 1475, 1220, 1170, 1065, 1040, 975, 915, 845; ms (dci NH_3) *m/z* (%) $[M+NH_4]^+$ 784 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.67 (1H, d, $J=16$ Hz, H-7″), 7.59 (2H, d, $J=9$ Hz, H-2″, H-6″), 7.13 (2H, d, $J=9$ Hz, H-3″, H-5″), 6.41 (1H, d, $J=16$ Hz, H-8″), 5.97 (1H, d, $J=1.5$ Hz, H-1), 5.26 (1H, dd, $J=10$ Hz, $J'=3$ Hz, H-3), 5.22 (1H, t, $J=9$ Hz, H-3′), 5.20 (1H, dd, $J=3$ Hz, $J'=1.5$ Hz, H-2), 5.14 (1H, t, $J=9$ Hz, H-4′), 4.99 (1H, t, $J=9$ Hz, H-2′), 4.71 (1H, d, $J=9$ Hz, H-1′), 4.46 (1H, dd, $J=12$ Hz, $J'=3$ Hz, H-6′b), 4.27 (1H, dd, $J=12$ Hz, $J'=5$ Hz, H-6′a), 3.84 (2H, m, H-5, H-5′), 3.69 (1H, t, $J=10$ Hz, H-4), 2.32 (3H, s, ArOAc), 2.15, 2.10, 2.08, 2.05, 2.02, 2.00 (6 × 3H, 6s, 6 × OAc), 1.36 (3H, d, $J=6$ Hz, Me-6); ^{13}C nmr see Table 1.

SYNTHESIS OF ALKALOID-GLYCOSIDES **3**, **4**, **5**, **13**, **14**, AND **15**.—In a typical experiment, freshly distilled stannic chloride (0.3 ml) was added dropwise under stirring to a solution of hordenine (165 mg, 1 mmol) and disaccharide **30**, **31**, **32**, **33**, **34**, or **35** (0.4 mmol) in dry MeCN. The reaction mixture was kept under stirring for 5 h at 20°, diluted with H_2O (20 ml), alkalinized by concentrated NH_3, filtered, and extracted by CH_2Cl_2 (3 × 30 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. Purification of the residue by flash chromatography [silica, CH_2Cl_2-MeOH-concentrated NH_3 (90:10:1, 85:15:1.5)] led to the corresponding alkaloid-glycoside in 50–60% yield.

(*E*)-HORDENINE-(2,3,4-TRI-*O*-ACETYL-6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSYL)-(1↦2)-3,4-DI-*O*-ACETYL-α-L-RHAMNOPYRANOSIDE [**3**].—Colorless glass: $[\alpha]^{20}D$ −41° ($CHCl_3$, $c=0.8$); uv ($CHCl_3$) λ max nm (log ε) 280 (4.47); ir (KBr) ν max cm^{-1} 2950, 1760, 1635, 1510, 1380, 1225, 1175, 1045, 985, 910, 775; ms (dci NH_3) *m/z* (%) $[M+H]^+$ 814 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.57 (1H, d, $J=16$ Hz, H-7‴), 7.39 (5H, m, H-2‴, H-3‴, H-4‴, H-5‴, H-6‴), 7.08 (2H, d, $J=9$

Hz, H-3, H-5), 6.97 (2H, d, J = 9 Hz, H-2, H-6), 6.29 (1H, d, J = 16 Hz, H-8‴), 5.58 (1H, d, J = 1.5 Hz, H-1′), 5.36 (1H, dd, J = 9 Hz, J' = 3 Hz, H-3′), 5.26 (1H, t, J = 9 Hz, H-3″), 5.13 (1H, t, J = 9 Hz, H-2″), 5.08 (1H, t, J = 9 Hz, H-4″), 4.98 (1H, t, J = 9 Hz, H-4′), 4.59 (1H, d, J = 9 Hz, H-1″), 4.27 (2H, m, H-6″a, H-6″b), 4.21 (1H, dd, J = 3 Hz, J' = 1.5 Hz, H-2′), 3.87 (1H, dq, J = 9 Hz, J' = 6 Hz, H-5′), 3.76 (1H, ddd, J = 9 Hz, J' = 6 Hz, J'' = 3 Hz, H-5″), 2.82 (2H, m, H_2-7), 2.73 (2H, m, H_2-8), 2.51 (6H, s, NMe_2), 2.17, 2.11, 2.04, 2.03, 2.01 (5 × 3H, 5s, 5 × OAc), 1.14 (3H, d, J = 6 Hz, Me-6′); ^{13}C nmr see Table 2.

(*E*)-HORDENINE-(2,3,4-TRI-*O*-ACETYL-6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSYL)-(1→3)-2,4-DI-*O*-ACETYL-α-L-RHAMNOPYRANOSIDE [**4**].—Colorless glass; $[\alpha]^{20}_D$ −34° ($CHCl_3$, c = 1); uv ($CHCl_3$) λ max nm (log ε) 282 (4.52); ir (KBr) ν max cm^{-1} 2950, 1760, 1640, 1510, 1380, 1225, 1175, 1065, 1040, 985, 910, 775; ms (dci NH_3) m/z (%) $[M+H]^+$ 814 (100); ^{1}H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.67 (1H, d, J = 16 Hz, H-7‴), 7.40 (2H, m, H-2‴, H-6‴), 7.28 (3H, m, H-3‴, H-4‴, H-5‴), 5.93 (2H, d, J = 9 Hz, H-3, H-5), 6.85 (2H, d, J = 9 Hz, H-2, H-6), 6.40 (1H, d, J = 16 Hz, H-8‴), 5.32 (1H, d, J = 2 Hz, H-1′), 5.31 (1H, dd, J = 3 Hz, J' = 2 Hz, H-2′), 5.15 (1H, t, J = 9 Hz, H-3″), 5.07 (1H, t, J = 9 Hz, H-4′), 5.03 (1H, t, J = 9 Hz, H-4″), 4.94 (1H, t, J = 9 Hz, H-2″), 4.69 (1H, d, J = 9 Hz, H-1″), 4.29 (2H, m, H-6″a, H-6″b), 4.21 (1H, dd, J = 9 Hz, J' = 3 Hz, H-3′), 3.81 (2H, m, H-5′, H-5″), 2.78 (2H, m, H_2-7), 2.67 (2H, m, H_2-8), 2.42 (6H, s, NMe_2), 2.06, 2.04, 1.97, 1.96, 1.92 (5 × 3H, 5s, 5 × OAc), 1.11 (3H, d, J = 6 Hz, Me-6′); ^{13}C nmr see Table 2.

The compound was identical with that obtained by acetylation of the natural alkaloid-glycoside previously isolated from *S. doederleinii* ($[\alpha]^{20}_D$, uv, ir, ms, ^{1}H nmr, tlc) (1).

(*E*)-HORDENINE-(2,3,4-TRI-*O*-ACETYL-6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSYL)-(1→4)-2,3-DI-*O*-ACETYL-α-L-RHAMNOPYRANOSIDE [**5**].—Colorless glass: $[\alpha]^{20}_D$ −40° ($CHCl_3$, c = 1); uv ($CHCl_3$) λ max nm (log ε) 280 (4.48); ir (KBr) ν max cm^{-1} 2950, 1760, 1640, 1510, 1375, 1250, 1220, 1170, 1070, 1045, 985, 910, 775; ms (dci NH_3) m/z (%) $[M+H]^+$ 814 (100); ^{1}H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.72 (1H, d, J = 17 Hz, H-7‴), 7.57 (2H, m, H-2‴, H-6‴), 7.42 (3H, m, H-3‴, H-4‴, H-5‴), 7.13 (2H, d, J = 9 Hz, H-3, H-5), 7.01 (2H, d, J = 9 Hz, H-2, H-6), 6.47 (1H, d, J = 17 Hz, H-8‴), 5.46 (1H, dd, J = 9 Hz, J' = 3 Hz, H-3′), 5.37 (1H, d, J = 1.5 Hz, H-1′), 5.33 (1H, dd, J = 3 Hz, J' = 1.5 Hz, H-2′), 5.21 (1H, t, J = 9 Hz, H-3″), 5.14 (1H, t, J = 9 Hz, H-4″), 4.99 (1H, t, J = 9 Hz, H-2″), 4.76 (1H, d, J = 9 Hz, H-1″), 4.70 (1H, dd, J = 12 Hz, J' = 3 Hz, H-6″b), 4.30 (1H, dd, J = 12 Hz, J' = 5 Hz, H-6″a), 3.88 (2H, m, H-5, H-5″), 3.74 (1H, t, J = 9 Hz, H-4′), 2.89 (2H, m, H_2-7), 2.76 (2H, m, H_2-8), 2.52 (6H, s, NMe_2), 2.14, 2.12, 2.08, 2.05, 2.03 (5 × 3H, 5s, 5 × OAc), 1.31 (3H, d, J = 6 Hz, Me-6′); ^{13}C nmr see Table 2.

(*E*)-HORDENINE-[6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSYL]-(1→2)-3,4-DI-*O*-ACETYL-α-L-RHAMNOPYRANOSIDE [**13**].—Colorless glass: $[\alpha]^{20}_D$ −29° ($CHCl_3$, c = 0.5); uv ($CHCl_3$) λ max nm (log ε) 283 (4.44), 290 (sh, 4.42); ir (KBr) ν max cm^{-1} 2950, 1760, 1635, 1510, 1375, 1225, 1170, 1045, 985, 910; ms (dci NH_3) m/z (%) $[M+H]^+$ 872 (100); ^{1}H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.58 (1H, d, J = 17 Hz, H-7‴), 7.49 (2H, d, J = 8 Hz, H-2‴, H-6‴), 7.13 (2H, d, J = 8 Hz, H-3‴, H-5‴), 7.08 (2H, d, J = 8 Hz, H-3, H-5), 6.97 (2H, d, J = 8 Hz, H-2, H-6), 6.29 (1H, d, J = 17 Hz, H-8‴), 5.58 (1H, d, J = 2 Hz, H-1′), 5.34 (1H, dd, J = 10 Hz, J' = 3 Hz, H-3′), 5.27 (1H, t, J = 9 Hz, H-3″), 5.12 (1H, t, J = 9 Hz, H-2″), 5.09 (1H, t, J = 9 Hz, H-4″), 4.98 (1H, t, J = 10 Hz, H-4′), 4.60 (1H, d, J = 9 Hz, H-1″), 4.27 (2H, m, H-6″a, H-6″b), 4.21 (1H, dd, J = 3 Hz, J' = 2 Hz, H-2′), 3.86 (1H, m, H-5′), 3.76 (1H, m, H-5″), 2.80 (2H, m, H_2-7), 2.72 (2H, m, H_2-8), 2.48 (6H, s, NMe_2), 2.34 (3H, s, ArOAc), 2.17, 2.11, 2.03, 2.02, 2.00 (5 × 3H, 5s, 5 × OAc), 1.16 (3H, d, J = 6 Hz, Me-6′); ^{13}C nmr see Table 2.

(*E*)-HORDENINE-[6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSYL]-(1→3)-2,4-DI-*O*-ACETYL-α-L-RHAMNOPYRANOSIDE [**14**].—Colorless glass: $[\alpha]^{20}_D$ −31° ($CHCl_3$, c = 1); uv ($CHCl_3$) λ max nm (log ε) 283 (4.42), 290 (sh, 4.41); ir (KBr) ν max cm^{-1} 2950, 1760, 1635, 1605, 1510, 1375, 1225, 1170, 1060, 1040, 990, 910, 840; ms (dci NH_3) m/z (%) 872 $[M+H]^+$ (100); ^{1}H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.72 (1H, d, J = 17 Hz, H-7‴), 7.48 (2H, d, J = 8 Hz, H-2‴, H-6‴), 7.06 (2H, d, J = 8 Hz, H-3‴, H-5‴), 7.00 (2H, d, J = 8 Hz, H-3, H-5), 6.68 (2H, d, J = 8 Hz, H-2, H-6), 6.41 (1H, d, J = 17 Hz, H-8‴), 5.39 (1H, d, J = 1.5 Hz, H-1′), 5.37 (1H, dd, J = 3 Hz, J' = 1.5 Hz, H-2′), 5.19 (1H, t, J = 9 Hz, H-3″), 5.12 (1H, t, J = 9 Hz, H-4′), 5.08 (1H, t, J = 9 Hz, H-4″), 4.99 (1H, t, J = 9 Hz, H-2″), 4.72 (1H, d, J = 9 Hz, H-1″), 4.31 (2H, m, H-6″a, H-6″b), 4.23 (1H, dd, J = 9 Hz, J' = 3 Hz, H-3′), 3.86 (2H, m, H-5′, H-5″), 2.87 (2H, m, H_2-7), 2.76 (2H, m, H_2-8), 2.51 (6H, s, NMe_2), 2.31 (3H, s, ArOAc), 2.14, 2.11, 2.04, 2.03, 2.00 (5 × 3H, 5s, 5 × OAc), 1.14 (3H, d, J = 6 Hz, Me-6′); ^{13}C nmr see Table 2.

The compound was identical with the product obtained by acetylation of natural **7** ($[\alpha]^{20}_D$, uv, ir, ms, ^{1}H nmr, tlc).

(*E*)-HORDENINE-[6-*O*-(4-ACETOXYCINNAMOYL)-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSYL]-(1↦4)-2,3-DI-*O*-ACETYL-α-L-RHAMNOPYRANOSIDE [**15**].—Colorless glass: $[\alpha]^{20}D$ −34° ($CHCl_3$, $c = 1$); uv ($CHCl_3$) λ max nm (log ε) 285 (4.45), 291 (sh, 4.44); ir (KBr) ν max cm^{-1} 2950, 1760, 1635, 1605, 1510, 1380, 1225, 1170, 1065, 1045, 985, 910, 840; ms (dci NH_3) *m/z* (%) $[M + H]^+$ 872 (100); ^1H nmr (270 MHz, $CDCl_3$, TMS) δ ppm 7.70 (1H, d, $J = 16$ Hz, H-7‴), 7.57 (2H, d, $J = 9$ Hz, H-2‴, H-6‴), 7.12 (2H, d, $J = 9$ Hz, H-3‴, H-5‴), 7.10 (2H, d, $J = 8$ Hz, H-3, H-5), 6.99 (2H, d, $J = 8$ Hz, H-2, H-6), 6.39 (1H, d, $J = 16$ Hz, H-8‴), 5.43 (1H, dd, $J = 9$ Hz, $J' = 3$ Hz, H-3′), 5.34 (1H, d, $J = 1.5$ Hz, H-1′), 5.32 (1H, dd, $J = 3$ Hz, $J' = 1.5$ Hz, H-2′), 5.19 (1H, t, $J = 9$ Hz, H-3″), 5.12 (1H, t, $J = 9$ Hz, H-4″), 4.98 (1H, t, $J = 9$ Hz, H-2″), 4.72 (1H, d, $J = 9$ Hz, H-1″), 4.46 (1H, dd, $J = 12$ Hz, $J' = 3$ Hz, H-6‴b), 4.26 (1H, dd, $J = 12$ Hz, $J' = 5$ Hz, H-6‴a), 3.86 (2H, m, H-5′, H-5″), 3.70 (1H, t, $J = 9$ Hz, H-4′), 2.92 (2H, m, H_2-7), 2.83 (2H, m, H_2-8), 2.56 (6H, s, NMe_2), 2.32 (3H, s, ArOAc), 2.11, 2.10, 2.04, 2.01, 1.99 (5 × 3H, 5s, 5 × OAc), 1.28 (3H, d, $J = 6$ Hz, Me-6′); ^{13}C nmr see Table 2.

(*E*)-HORDENINE-[6-*O*-(4-HYDROXYCINNAMOYL)-β-D-GLUCOPYRANOSYL]-(1↦3)-α-L-RHAMNOPYRANOSIDE [**7**].—Isolated by cc on Si gel from the most polar fractions of the *n*-BuOH extract of *S. doederleinii* (1) as an amorphous solid: $[\alpha]^{20}D$ −81° (MeOH, $c = 0.2$); uv (MeOH) λ max nm 227, 315, (MeOH + MeONa) λ max nm 227, 243 (sh), 312 (sh), 365; ms (dci NH_3) *m/z* (%) $[M + H]^+$ 620 (11), 474 (12), 312 (13), 166 (100); ^1H nmr (270 MHz, CD_3SOCD_3, TMS) δ ppm 7.57 (1H, d, $J = 16$ Hz, H-7‴), 7.20 (2H, d, $J = 9$ Hz, H-2‴, H-6‴), 6.93 (2H, d, $J = 9$ Hz, H-3‴, H-5‴), 6.76 (2H, d, $J = 9$ Hz, H-3, H-5), 6.70 (2H, d, $J = 9$ Hz, H-2, H-6), 6.38 (1H, d, $J = 16$ Hz, H-8‴), 5.28 (1H, d, $J = 2$ Hz, H-1′), 4.52 (1H, d, $J = 8$ Hz, H-1″), 4.40 (1H, m, H-6″a), 4.18 (1H, m, H-6″b), 4.02–3.31 (8H, m, H-2′, H-4′, H-5′, H-2″, H-3″, H-4″, H-5″), 2.86 (4H, m, H_2-7, H_2-8), 2.79 (6H, s, NMe_2), 1.12 (3H, d, $J = 6$ Hz, Me-6′).

ACETYLATION OF **7**.—To a solution of **7** (8 mg) in pyridine (1 ml) was added Ac_2O (1 ml). The mixture was kept at 20° for 72 h. After removal of the reagents and purification by cc, **14** was obtained as a glassy solid (5 mg), identical with the synthetic sample described above.

(*E*)-HORDENINE-(6-*O*-CINNAMOYL-β-D-GLUCOPYRANOSYL)-(1↦3)-α-L-RHAMNOPYRANOSIDE [**6**].—The ^{13}C-nmr spectrum of **6** previously published (1) has to be reassigned as follows: δ ppm 17.6 (C-6′), 32.1 (C-7), 44.8 (2C, NMe_2), 60.6 (C-8), 64.0 (C-6″), 69.6 (C-5′), 70.1 (C-2′), 70.3 (C-4″), 70.4 (C-4′), 73.6 (C-5″*), 73.7 (C-2″*), 76.0 (C-3″), 80.9 (C-3′), 98.6 (C-1′), 104.6 (C-1″), 116.3 (2C, C-2, C-6), 117.7 (C-8‴), 128.0 (2C, C-2‴, C-8‴), 128.7 (2C, C-3‴, C-5‴), 129.3 (2C, C-3, C-5), 130.1 (C-4‴), 133.6 (C-1‴**), 133.7 (C-4**), 144.4 (C-7‴), 154.0 (C-1), 165.9 (C-9‴). Assignments with the same superscript may be interchanged.

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