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IRIDOID MONO- AND DI-GLYCOSIDES IN *MENTZELIA**

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Key Word Index—*Mentzelia*; Loasaceae; iridoid glycosides; allose; mentzelose; quinovose; deutzioside; epoxydecaloside; loganin; secoiridoids; scopolin; iridoid aglucone; mentzetriol; ^{13}C NMR data; chemotaxonomy; biosynthetic considerations.

Abstract—Eight species of *Mentzelia* (Loasaceae) have been investigated for iridoid glycosides. In addition to the known glucosides deutzioside, decaloside, mongolioside, loganin and sweroside, several novel compounds have been isolated and characterized by chemical and spectroscopic means. 6′-*O*-Acetyl deutzioside was found in a single species, while the diglycosidic compounds glucosyl-decaloside, allosyl-decaloside and quinovosyl-decaloside were each isolated from one or more species. In addition, a novel compound, epoxydecaloside (= 11-hydroxy-deutzioside), together with glucosyl-epoxydecaloside, allosyl-epoxydecaloside and mentzelosyl-epoxydecaloside are described. The last compound contains a 4-deoxy-α-L-*erythro*-pentopyranosyl moiety, whose parent sugar, named mentzelose, has not been encountered so far in nature. A non-glycosidic iridoid, mentzetriol, has been characterized solely by spectroscopic means and a structure is proposed. The secoiridoid secoxyloganin has been found for the first time in a plant source, and the coumarin glucoside scopolin has been isolated from two species of *Mentzelia*. ^{13}C and ^{1}H NMR spectra of several iridoid compounds are presented. The biosynthesis of the compounds is considered and the systematic position of Loasaceae discussed concluding in a possible derivation from Cornalean ancestors.

INTRODUCTION

Previous investigations [1–4] have shown that iridoid glucosides occur in several genera and species within the angiospermous family Loasaceae. Danielson *et al.* [1, 2] first reported the isolation of deutzioside (='mentzeliosside' **1**)† and decaloside (**12**) from *Mentzelia decapetala* and later showed that additional iridoids were present [3]. Loganin (**24**) was isolated by Kooiman [4] from seeds of *Blumenbackia hieronymi* and shown to be present also in seeds and leaves of four other species from the family, including *Mentzelia lindleyi*.

We have now investigated 27 species from 10 genera within Loasaceae, and here report the results obtained with 8 species of *Mentzelia*. In addition to the known compounds **1** and **12**, several novel glycosides were isolated and characterized. The majority of these were derived from epoxydecaloside (**4** = 11-hydroxy-deutzioside) and decaloside (**12**) and contained an additional sugar (glucose, allose, quinovose or mentzelose, a novel 4-deoxy-pentose) attached to the 11-oxymethylene group.

RESULTS

Deutzioside (**1**) [1, 6] was isolated from *M. albescens* and *M. involucrata* (Table 3); 6′-*O*-acetyl deutzioside (**3**), was isolated in very small quantity from *M. albescens* only. The ^{1}H NMR spectrum of **3** showed only few differences from that of **1**, i.e. the presence of an acetyl group (δ 2.11) and a downfield shift of the 6′-CH_2-O signals from *ca* 3.8 (in **1**) to 4.33 (in **3**) proving the attachment of the acetyl group. The ^{13}C NMR data (Table 1) confirm this point. Thus, in **3** C-5′ was shifted upfield (2.1 ppm) and C-6′ downfield (2.4 ppm) relative to **1**. A synthetic sample of **3** was prepared by partial acetylation of **1**.

Epoxydecaloside (= 11-hydroxy-deutzioside, **4**) was isolated from *M. lindheimerii*. Its structure was deduced by comparison of its NMR spectra with those of the known compounds **1** and **12**. The ^{1}H NMR spectrum of **4** resembled that of **1**, except that the signal from the 11-Me group was replaced by a two-proton signal at δ 4.07 (*br. s*). The signals from H-3 and H-5 also showed minor downfield shifts (0.3 and 0.2 ppm, respectively), while the remaining signals and all the coupling constants were virtually identical in **1** and **4**. When comparing the ^{13}C NMR spectra of **1** and **4**, major differences were found for C-3, C-4, C-5 and C-11, as would be expected by the introduction of a hydroxy group at C-11. On the other hand the shifts, except for that of C-5, were similar to those of **12**, having the same functionality at C-11. The different C-5 signal was accounted for by the different functionalities in the cyclopentane rings of **4** and **12**. Attempts to prepare **2** from **5** by hydrogenolysis (H_2, Pd/C in HOAc or EtOH) gave rise to a mixture consisting mainly of 3,4-dihydro compounds, as seen from the ^{1}H NMR spectra. Likewise, in an attempt to epoxidize the 7,8-double bond of **13** (*m*-CPB in CH_2Cl_2), after 24 hr no reaction was observed. The spectroscopic evidence, however, indicated the same stereochemistry for all centres in **1**, **4** and **12**.

* Part I in the series "Iridoids in Loasaceae".

† Deutzioside isolated in pure state from seven species of *Deutzia* (Hydrangeaceae) by Plouvier [5] in 1965 is identical with the subsequently described mentzelioside [6], the latter name thus becoming redundant.

Table 1. ^{13}C NMR data* for the *Mentzelia* iridoids

	1	3†	4	6	8	10	12	14	16	18	Methyl-β-D-quinovo-pyranoside‡
C-1	96.8	96.8	96.9	97.0	97.0 (*d* 168)	96.9 (*d* 166)	97.9 (*d* 174)	98.5	98.5 (*d* 174)	98.7 (*d* 173)	
C-3	135.7	135.8	139.9	142.2	142.2 (*d* 193)	141.7 (*d* 189)	139.3 (*d* 188)	141.6	141.6 (*d* 189)	141.7 (*d* 188)	
C-4	113.5	113.3	115.8	111.9	111.8 *s*	112.2 *s*	116.7 *s*	113.3	113.5 *s*	113.6 *s*	
C-5	41.1	41.0	37.9	38.2	38.3 (*d* 136)	38.6 (*d* 135)	43.6 (*d* 135)	44.6	44.7 (*d* 136)	44.9 (*d* 135)	
C-6	78.6	78.5	78.6	78.1	78.0 *d*	78.1 (*d* 144)	81.0 (*d* 146)	80.9	81.0 (*d* 148x)	81.2 (*d* 146x)	
C-7	59.7	59.3	59.1	59.4	59.3 (*d* 190)	59.3 (*d* 195x)	135.9 (*d* 168)	136.1	136.1 (*d* 167)	136.2 (*d* 166)	
C-8	56.6	56.2	56.2	56.2	56.1 (*d* 194)	56.1 (*d* 194x)	134.5 (*d* 170)	134.2	134.2 (*d* 167)	134.2 (*d* 166)	
C-9	42.6	42.5	42.1	42.2	42.2 (*d* 140)	42.2 (*d* 139)	47.7 (*d* 135)	47.7	47.7 (*d* 136)	47.8 (*d* 138)	
C-11	16.0	16.1	62.0	69.7	69.6 (*t* 146)	69.8 (*t* 149)	61.9 (*t* 144x)	70.3	70.1 (*t* 146x)	70.5 (*t* 148x)	
C-1′	100.0	100.1	99.9	100.0	100.1 (*d* 164)	100.0 (*d* 162x)	99.3 (*d* 162)	99.4	99.7 (*d* 162)	99.6 (*d* 161)	
C-2′	73.5	73.5	73.5	73.5	73.5	73.5	73.5	73.4	73.5	73.6	
C-3′	76.6	76.4	76.6	76.7	76.6	76.5	76.5	76.6	76.5	76.6	
C-4′	70.3	70.2	70.3	70.5	70.3	70.3	70.3	70.3	70.4	70.5	
C-5′	77.1	74.5	77.1	77.1	77.1	77.1	77.0	77.1	77.1	77.2	
C-6′	61.4	63.8	61.4	61.6	61.4	61.4	61.4	61.4	61.5	61.5	
C-1″				101.5	99.2 (*d* 164)	99.8 (*d* 162x)		101.8	99.4 (*d* 162)	101.9 (*d* 161)	104.3
C-2″				74.0	71.2	69.4 (*d*)		74.0	71.2	74.2 *d*	74.5
C-3″				76.7	72.0	68.5 (*d* 145)		76.4	72.0	76.7 *d*	76.7
C-4″				70.5	67.7	29.2 (*t* 129)		70.3	67.7	75.8 *d*	76.2
C-5″				76.7	74.5	60.2 (*t* 148x)		76.4	74.4	72.6 *d*	73.0
C-6″				61.6	62.1			61.4	62.1	17.6 (*q* 126)	17.8

* Spectra of glycosides (D_2O, dioxan) and acetates ($CDCl_3$, TMS) were recorded at 22.6 MHz unless otherwise noted [12].
† D_2O–acetone-d_6 was used as solvent.
‡ Data from ref. [9].
§ Data from ref. [10]. The shift for C-10 in **22** is 66.2, *t* (140) and 67.6 in **23**.
‖ Recorded at 67.9 MHz.

In addition to **1**, **3** and **4**, three more compounds (**6**, **8** and **10**) having the 7,8-epoxy functionality were isolated from various species of *Mentzelia*. They were characteristic in having very low R_f values in the solvent systems used for separation. The ^{1}H NMR signals of H-3 and 11-CH_2 (Table 2) can be used to distinguish between these compounds and those of lower molecular weight.

The main constituent from *M. lindheimerii* contained two β-glucopyranosyl moieties as deduced from the NMR spectra. The structure of the new compound, glucosyl-epoxydecaloside (**6**), was demonstrated by comparison with the ^{13}C NMR spectrum of **4**. The spectrum of **6** was readily assigned, showing, besides the presence of an additional β-glucopyranosyl moiety, very good correspondence for all signals except for those from C-3, C-4 and C-11. The large downfield shift for the latter in **6** (7.7 ppm relative to **4**) demonstrated that this was the position of attachment for the additional glucopyranosyl moiety. Acetylation gave rise to a nonaacetate (**7**), in agreement with the proposed structure.

An isomer, allosyl-epoxydecaloside (**8**), isolated from *M. albescens*, again yielded a nonaacetate (**9**) by acetylation. The ^{13}C NMR spectra of **8** and **9** were virtually coincident with those of **6** and **7**, except for a set

Table 1. (*Continued*)

	20	**22** §	**2**	**5**‖	**7**	**9**	**11**‖	**13**	**15**‖	**17**	**19**	**23**§
C-1	65.8 (*t* 149)	97.4 (*d* 169)	95.5 (*d* 165)	95.6	96.2	95.9 (*d* 160)	95.7 (*d* 163)	96.6 (*d* 166x)	95.8	96.0 (*d* 167x)	96.1 (*d* 164x)	94.0
C-3	111.1 (*t* 157)	134.3 (*d* 182)	136.3 (*d* 189)	142.4	140.8	140.5 (*d* 189)	140.7 (*d* 188)	141.4 (*d* 190)	140.0	140.0 (*d* 191x)	140.1 (*d* 189)	133.9
C-4	154.4 *s*	115.8 *s*	110.4 *s*	109.4	110.9	111.4 *s*	110.5 *s*	110.9 *s*	110.9	111.5 *s*	111.4 *s*	112.6
C-5	48.7 (*d* 136)	38.9 (*d* 133)	37.7 (*d* 136)	34.8	33.8	33.8 (*d* 138)	34.7 (*d* 137)	40.8 (*d* 135x)	39.8	40.1 (*d* 137)	40.1 (*d* 137x)	36.8
C-6	78.5 (*d* 145x)	30.2 (*t* 130)	79.8 (*d* 149x)	79.1	79.6	79.6 (*d* 149x)	79.3 (*d* 149)	82.2 (*d* 150x)	81.5	81.8 (*d* 150x)	82.0 *d*	26.7
C-7	135.6 (*d* 166)	27.8 (*t* 128)	55.0 (*d* 193)	54.7	54.8	54.8 (*d* 193)	54.6 (*d* 192)	132.2 (*d* 170)	131.7	131.9 (*d* 171x)	132.0 (*d* 169)	27.9
C-8	135.0 (*d* 166)	43.2 (*d* 128)	55.1 (*d* 193)	54.9	54.8	55.0 (*d* 193)	54.8 (*d* 193)	135.5 (*d* 167)	135.8	136.1 (*d* 170)	136.0 (*d* 166)	38.2
C-9	53.1 (*d* 125)	45.0 (*d* 131)	41.3 (*d* 141)	40.8	41.0	41.2 (*d* 142)	40.7 (*d* 141)	46.8 (*d* 138x)	46.7	47.0 (*d* 138)	46.9 (*d* 140x)	45.3
C-11	63.0 (*t* 143)	16.0 (*q* 125)	15.9 (*q* 128)	63.4	69.0	68.8 (*t* 145x)	68.0 (*t* 145)	64.0 (*t* 148)	68.8	69.0 (*t* 145x)	68.8 *t*	15.7
C-1′		99.5 (*d* 161)	97.2 (*d* 165)	97.2	97.3	97.3 (*d* 164)	97.2 (*d* 163)	96.6 (*d* 166x)	96.0	96.3 (*d* 165x)	96.1 (*d* 164x)	95.6
C-2′		73.7	70.8	70.6	70.8	70.9	70.6	70.8	70.5	70.7	70.7	70.8
C-3′		76.6	72.1	72.1	72.1	72.3	72.0	72.1	71.7	72.2	72.2	72.0
C-4′		70.4	68.3	68.0	68.2	68.4	68.2	68.3	68.1	68.5	68.4	68.4
C-5′		77.0	72.6	72.4	72.6	72.6	72.4	72.7	72.4	72.7	72.7	72.6
C-6′		61.6	61.7	61.4	61.6	61.7	61.4	61.8	61.6	61.9	61.9	61.9
C-1″					100.9	99.1 (*d* 163)	97.6 (*d* 159)		99.8	98.3 (*d* 164)	100.0 (*d* 159)	
C-2″					71.3	68.8	68.0 (*d* 154x)		71.2	69.3	71.9 *d*	
C-3″					72.3	68.8	68.1 (*d* 154x)		71.9	68.7	73.1 *d*	
C-4″					68.2	66.4	26.5 (*t* 130)		68.2	66.4	73.5 *d*	
C-5″					72.6	70.2	59.8 (*t* 144)		72.8	70.3	70.1 *d*	
C-6″					61.6	62.4			61.8	62.4	17.5 (*q* 126)	

of signals arising from a β-allopyranosyl moiety (Table 1) as seen by comparison with the spectra of β-D-allopyranose and methyl tetra-*O*-acetyl-β-D-allopyranoside [7]. Cleavage of **9** with boron trifluoride etherate in acetic anhydride gave, as the sole isolable compound, penta-*O*-acetyl-β-allopyranose, identified by ^{1}H NMR. The preparation was not pure and showed no significant optical rotation. The same plant contained, however, allosyl-decaloside (**16**, see below); in the latter case the sugar moiety attached to the 11-position was shown to be β-D-allopyranose. Furthermore, a small but significant difference was found between the ^{13}C NMR signals arising from the glucopyranosyl moieties attached to C-1 and those attached to C-11 (Table 1). In the case of compound **8**, the ^{13}C NMR spectrum clearly proved that the iridoid moiety carried the glucopyranosyl group at C-1 and thus the allopyranosyl group at C-11.

The third diglycoside (**10**) was isolated from *M. involucrata* and contained one carbon atom less than **6** and **8**. Acetylation gave rise to a heptaacetate (**11**) showing the presence of only seven hydroxy groups in the molecule. Comparison of the ^{13}C NMR spectra of **10** and **11** with the known compounds above proved the presence (Table 1) of a deutziosyl moiety substituted with a deoxypentopyranosyl moiety. The coupling constant of the anomeric carbon (162 Hz in **10** and 159 Hz in **11**) showed the presence of an equatorial linkage to the iridoid part of the molecule [8]. The triplet at δ 29.2 in **10** was shifted upfield (2.7 ppm) after acetylation, showing the presence of only one hydroxy group on the α-carbon atoms, and suggesting that the sugar was a 4-deoxypentose. The ^{1}H NMR spectra recorded at 270 MHz confirmed this assignment. Decoupling experiments showed that H-2″ and H-3″ resonated at low field while the multiplet at high field could be ascribed to 4″-CH_2. Moreover, as H-1″ had already been shown by the ^{13}C NMR spectrum to be axial, the small coupling constant, $J_{1'',2''} = 1.5$ Hz, was an ax–eq coupling proving that the 2″-OH substituent was in the axial position. This left the configuration of the 3″-OH group to be determined. The coupling constant $J_{2'',3''}$

Table 2. ^{1}H NMR data* for the *Mentzelia* iridoids

	1	**3**	**4**	**6**	**8**	**10†**	**12**	**14**	**16**	**18**	**20†**
H-1	4.80 (*d* 10)	4.78 (*d* 10)	4.89 (*d* 10)	4.96 (*d* 9.5)	4.97 (*d* 9.5)	4.94 (*d* 9.5)	5.09 (*d* 5.5)	5.06 (*d* 6)	5.06 (*d* 6)	5.05 (*d* 6)	3.38 (7.5) 3.46 (5.5) (AB 11)
H-3	6.15 *m*	6.17 *m*	6.42 *m*	6.54 *m*	6.55 *m*	6.51 *m*	6.36 *m*	6.48 *m*	6.48 *m*	6.49 *m*	5.15 5.27 *br. s*'s
H-5	2.07 (*t* 7.5)	2.06 n.r.	2.28 (*t* 7.5)	2.35 (*t* 7.5)	2.32 (*t* 7.5)	2.29 (*t* 7.5)	2.75 *m*	2.76 *m*	2.78 (*m* 4; 7.5)	2.80 *m*	2.69 (*t* 7.5)
H-6	4.12 (*dd* 7.5; 1.5)	4.12 (*dd* 7.5; 1.5)	4.11 (*br. d* 7.5)	4.22 (*dd* 8; 4.5)	4.2 n.r.	4.15 (*br. d* 7.5)	4.7 n.r.		4.7 n.r.	4.7 n.r.	5.12 (*dd* 8; 1.5)
H-7	3.62 (*dd* 2.5; 1.5)	3.62 *m*	3.63 *m*	3.68 *m*	3.69 *m*	3.66 *m*					
							6.01 *m*	6.01 *m*	6.03 *m*	6.03 *m*	5.92 *m*
H-8	3.73 (*d* 2.5)	3.68 (*d* 3)	3.73 n.r.	3.79 n.r.	3.78 (*d* 3)	3.77 (*d* 3)					
H-9	2.55 (*dd* 9.5; 7.5)	2.55 (*dd* 10; 8)	2.54 (*dd* 9; 7.5)	2.52 (*dd* 9.5; 7.5)	2.59 (*dd* 9.5; 7.5)	2.60 (*dd* 9.5; 7.5)	3.15 n.r.	3.15 n.r.	3.12 (*dd* 8; 6)	3.13 *m*	3.02 *m*
						4.13	4.01				
H-11	1.64 *s*	1.63 *s*	4.05 *m*	4.30 *m*	4.29 *m*	4.23 (AB 11.5)	4.21 (AB 12)	4.32 *m*	4.32 *m*	4.32 *m*	4.07 *m*
H-1″				4.50 (*d* 7.5)	4.7 n.r.	4.61 (*d* 1.5)		4.49 (*d* 7.5)	4.7 n.r.	4.51 (*d* 7.5)	

* Spectra recorded at 90 MHz in D_2O (DSS) for glycosides or in $CDCl_3$ (TMS) for acetates, unless otherwise indicated; n.r. = not resolved.
† Recorded at 270 MHz.
‡ Data from ref. [10].

Table 2. (*Continued*)

	22‡	**2**	**5**	**7**	**9**	**11**†	**13**	**15**	**17**	**19**	**21**	**23**‡
H-1	5.13 (*d* 4)	4.57 (*d* 9)	4.63 n.r.	4.62 n.r.	4.65 n.r.	4.64 (*d* 9)	4.90 (*d* 5)			4.93 *d*	3.82(6) 4.08(5) (AB 11)	5.20 *br. s*
H-3	6.10 *br. s*	6.06 *m*	6.43 *m*	6.33 *m*	6.40 *m*	6.36 *m*	6.38 *m*	6.29 *m*	6.35 *m*	6.28 *m*	5.12 5.25 *br. s*'s	6.00 *m*
H-5	2.45 *m*	2.29 (*t* 8)	2.5 *m*	2.5 *m*	2.55 *m*	2.52 *m*	2.85 *m*	2.82 *m*	2.86 *m*	2.84 *m*	2.93 (*dd* 6; 8)	2.53 *m*
H-6		4.92 (*dd* 8; 1.5)	4.9 n.r.			4.85 (*br. d* 7)	5.58 *m*	5.59 *m*	5.6 *m*	5.58 *m*		
H-7		3.63	3.63	3.63	3.66	3.68 (*dd* 2.5; 0.7)	5.94 (*dt* 6; 1.5)	5.93 *dt*	5.95 *dt*	5.95 *dt*	5.92 n.r.	
H-8		*m*	*m*	*m*	*m*	3.62 (*d* 2.5)	6.08 (*dd* 6; 1.5)	6.05 *dd*	6.08 *dd*	6.07 *dd*		
H-9		2.48 (*dd* 9; 8)	2.5 n.r. 4.26	2.5 n.r.	2.55 n.r.	2.52 n.r. 3.86	3.09 *m* 4.40	3.11 *m*	3.15 *m*	3.12 *m* 4.04	3.19 *m*	
H-11	1.55 *s*	1.52 *br. s*	4.58 (AB 12)	4.18 *br. s*	4.2 *br. s*	4.14 (AB 12)	4.69 (AB 12)	4.2 *m*	4.2 *m*	4.23 (AB 11)	4.46 *br. s*	1.52 *br. s*
H-1″				4.41 (*d* 7)	4.70 (*d* 8)	4.47 (*d* 1.2)		4.52 (*d* 7)		4.47 (*d* 7)		

= *ca* 2 Hz could indicate either ax–eq or eq–eq coupling, but as one of the 3″,4″-couplings was estimated to be >8 Hz (ax–ax coupling), the 3″-OH group must be equatorial, defining the structure of the sugar moiety as a 4-deoxy-α-*erythro*-pentopyranosyl radical with unknown absolute configuration. Cleavage of **11**, using somewhat milder conditions than those used for **9**, gave rise to two major products, namely **5**, whereby compounds **4** and **10** (together with **6** and **8**) were structurally inter-related, and an anomeric mixture of acetylated sugars. Deacetylation of this mixture followed by reduction and benzoylation gave rise to tetra-*O*-benzoyl-2-deoxy-D-*erythro*-pentitol identical with an authentic sample prepared from 2-*deoxy*-D-*erythro*-pentose (= 2-deoxy-D-ribose). Consequently, the C-11 sugar moiety of **10** was a 4-deoxy-α-L-*erythro*-pentopyranosyl unit, not previously encountered in natural products. We have named the novel sugar mentzelose in order to use the semi-systematic name mentzelosyl-epoxydecaloside for **10**.

The known compound decaloside (**12**) was encountered in four species of *Mentzelia*. The data for **12** and for the hexaacetate **13** showed good agreement with those reported [2]. As with **4**, three additional glycosylated derivatives of decaloside have been isolated and characterized.

The main glycoside (**14**) in *M. lindleyi* could not be obtained in the pure state, and was characterized by its NMR spectra only. Acetylation gave rise to a nonaacetate (**15**), which could be purified and crystallized. Comparison of **14**/**15** with **12**/**13** revealed the same relationship as between **6**/**7** and **4**/**5**, and allowed the assignment of **14** as glucosyl-decaloside with the additional glucopyranosyl moiety attached to C-11 of decaloside.

Allosyl-decaloside (**16**) was obtained as the main constituent of mature plants of *M. albescens*. Again, ^{13}C NMR spectra of **16** and the nonaacetate **17**, on comparison with spectra of the above compounds, disclosed the structure. Cleavage of **17** under the conditions previously used gave rise to penta-*O*-acetyl-β-D-allopyranose, proving the nature of the carbohydrate moiety. Apart from unconverted **17**, decaloside hexaacetate (**13**) was the only other product isolated from the reaction; thus, **16** contained a decalosyl moiety.

The third glycosylated derivative of decaloside, quinovosyl-decaloside (**18**), was isolated from *M. lindleyi*. The major constituents of this plant were **12**, **14** and **18**. Compounds **12** and **18** together with two minor compounds had almost identical R_f values on TLC with the eluants tested. However, by repeated chromatography, isolation of the major part of **12** and **18** was achieved. The ^{1}H NMR spectrum of **18** was reminiscent of that of **14**, except for a three-proton doublet at δ 1.31 and the absence of a 6-CH_2-OH signal at 3.8. This suggested that quinovose (= 6-deoxyglucose) might be a constituent of **18**. The ^{13}C NMR spectra of **18** and of the octaacetate **19** showed signals in full accord with this, and comparison of the former with that of methyl-β-D-quinovopyranoside [9] (Table 1) showed very good correspondence except for the expected difference for C-1″. Finally, cleavage as above gave tetra-*O*-acetyl-β-D-quinovopyranose in addition to decaloside hexaacetate (**13**). The two minor components of *M. lindleyi* also had absorptions at high field in the ^{1}H NMR spectrum (δ 1.35, *d* and 1.40, *d*, respectively) suggesting the presence of decaloside with 6-deoxy sugars attached at the 11-position. Due to difficulties in the separation and to lack of material these compounds were not isolated.

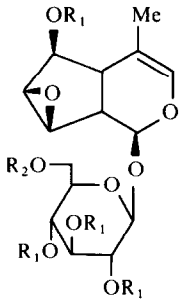
Several of the investigated plants contained a non-glycosidic iridoid spectroscopically reminiscent of some of the glycosides above. This compound was obtained only in small amount. A tentative structure (**20**) was deduced, based on the overall similarity of the NMR spectra (Tables 1 and 2) to those of decaloside (**12**). A triacetyl derivative (**21**) was formed by acetylation, and we have named the compound mentzetriol (**20**). The mass spectrum (see Experimental) was in excellent agreement with the proposed structure.

In addition to the typical C-10 deficient *Mentzelia* compounds described above, a few more previously known iridoid glucosides were found in the genus. Thus, mongolioside (**22**) was isolated from two species; it was identified by the NMR spectra and by conversion to the crystalline pentaacetate (**23**) [10]. Loganin (**24**) and the secoiridoids sweroside (**25**) and secoxyloganin (**26**) were each found in one, two and one species, respectively. The latter compound has been synthesized [11] from secologanin (**30**), but has not been reported as a plant constituent. Secoxyloganin (**26**) was not isolated in a pure state but was solely characterized by its ^{1}H NMR spectrum. Methylation with diazomethane gave rise to dimethyl secologanoside (**27**) which was acetylated to give the known crystalline tetraacetate (**28**). That **26** was indeed the 11-methyl ester and not the 7-methyl ester **29**, was shown by comparison of the ^{1}H NMR spectra of **26** and **27** and of secologanin tetraacetate (**31**) and **28**. In both cases the methyl signals (δ 3.69 and 3.68, respectively) of the mono-methyl esters coincided with the low field signal (3.69 and 3.68, respectively) of the dimethyl esters (**27** and **28**), showing that this arises from the α,β-unsaturated ester functionality at C-11.

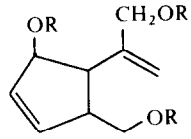
DISCUSSION

Glucose has until recently been regarded as the sole and obligatory sugar in iridoid glycosides [13]. Recently, however, a few examples have been reported of other sugars being attached to a iridoid moiety, namely xylose in montinioside [14], allose and xylosylallose in opulus iridoid I–IV [7], and rhamnose in α-L-rhamnopyranosylcatalpol [15]. The opulus iridoids carry an acyl group at C-1 and no glucose at all, while the remaining examples, including those reported in the present work, are all 1-glucosides. Seven examples of iridoid glucosides carrying an additional molecule of glucose have been reported, namely melittoside [16], 5-*O*-β-glucosyl-antirrhinoside [17], 10-*O*-β-glucosyl-aucubin [18], genipin-1-β-gentiobioside [19], kanokoside C and D [20] (both 11-gentiobiosides), and ulmoside (aucubigenin-1-β-isomaltoside) [21], see also Note Added in Proof.

The first report of allose as a constituent of vascular plants was by Perold *et al.* [22]. Since then several occurrences in a variety of sources have been published [7, 10, 23, 24]. The detection of allose as a constituent in glycosides is obviously a consequence of the use of NMR spectroscopy on the parent compounds and degradation products. The traditional methods of hydrolysis, followed by detection of the glycone by TLC or paper chromatography will not allow distinction between glucose and allose with most of the commonly used solvent systems (cf. [24]).



1 $R_1 = R_2 = H$
2 $R_1 = R_2 = Ac$
3 $R_1 = H$; $R_2 = Ac$



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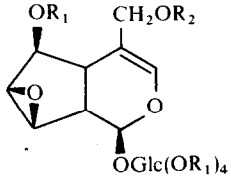
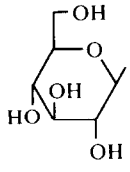
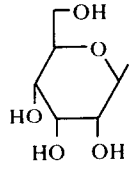
21 R = Ac



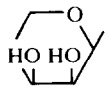
4 $R_1 = R_2 = H$
5 $R_1 = R_2 = Ac$
6 $R_1 = H$; $R_2 = Glc(OH)_4$
7 $R_1 = Ac$; $R_2 = Glc(OAc)_4$
8 $R_1 = H$; $R_2 = All(OH)_4$
9 $R_1 = Ac$; $R_2 = All(OAc)_4$
10 $R_1 = H$; $R_2 = Men(OH)_2$
11 $R_1 = Ac$; $R_2 = Men(OAc)_2$



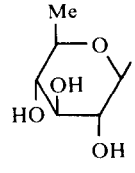
$Glc(OH)_4$



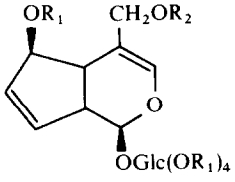
$All(OH)_4$



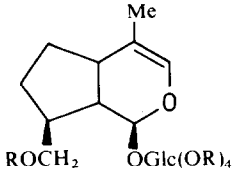
$Men(OH)_2$



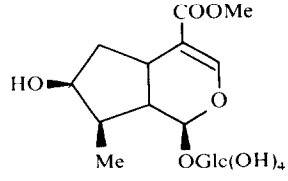
$Qui(OH)_3$



12 $R_1 = R_2 = H$
13 $R_1 = R_2 = Ac$
14 $R_1 = H$; $R_2 = Glc(OH)_4$
15 $R_1 = Ac$; $R_2 = Glc(OAc)_4$
16 $R_1 = H$; $R_2 = All(OH)_4$
17 $R_1 = Ac$; $R_2 = All(OAc)_4$
18 $R_1 = H$; $R_2 = Qui(OH)_3$
19 $R_1 = Ac$; $R_2 = Qui(OAc)_3$



22 R = H
23 R = Ac



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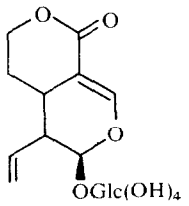

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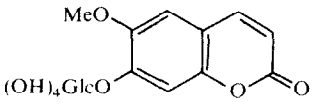

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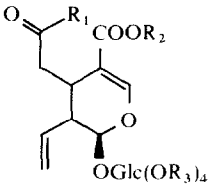


26 $R_1 = OH$; $R_2 = Me$; $R_3 = H$
27 $R_1 = OMe$; $R_2 = Me$; $R_3 = H$
28 $R_1 = OMe$; $R_2 = Me$; $R_3 = Ac$
29 $R_1 = OMe$; $R_2 = R_3 = H$
30 $R_1 = H$; $R_2 = Me$; $R_3 = H$
31 $R_1 = H$; $R_2 = Me$; $R_3 = Ac$

Apparently *Mentzelia* is the only genus within Loasaceae that contains iridoid glycosides lacking the C-10 carbon atoms. We have examined nine of the remaining fourteen genera [25], and loganin and/or secoiridoids are consistently found [26]. This combination of compounds in a family is otherwise found only in Hydrangeaceae [13]: *Hydrangea* contains loganin and secoiridoids and *Deutzia* contains deutzioside (**1**) and scabroside (= 5-OH-deutzioside). On the other hand, the compounds found in the present investigation are somewhat reminiscent of those found in *Viburnum* (Sambucaceae *sensu* Dahlgren [27]). Many species within this large genus contain iridoid-11-glycosides with glucose or allose [10], a feature not often encountered in iridoids. Furthermore, a few species of *Viburnum* contain loganin and/or secoiridoids [10]. Mongolioside (**22**) has so far been found only in this genus. Hydrangeaceae and Sambucaceae are both included in Dahlgren's [27] Cornales, while the systematic position and even homogeneity of Loasaceae has been much disputed by taxonomists (cf. [28]). Chemically, a derivation of Loasaceae from Cornalean ancestors is suggested, and the relationship is perhaps stronger than indicated in the system of Dahlgren.

The biosynthesis of deutzioside, (**1**) has been investigated in *Deutzia crenata* [29], and it was shown that iridodial glucoside (**33**) was a precursor of **1**. Mongolioside (**22**, = 10-OH-iridodial glucoside) thus becomes a possible intermediate on the route to the probable common precursor of **1** and **12**, namely 11-deoxydecaloside (**34**). The formation of **6** and **14** could easily be explained by glucosylation of **4** and **12**, respectively.

Direct glycosylation in the biosynthesis of **8**, **10**, **16** and **18** is not without problems, however, even though it is known that some sugars, for example apiose [30], are formed separately as a nucleoside sugar pyrophosphate before attachment to an aglycone to form a glycoside [31]. The present finding that young plants of *M. albescens* contain the 11-glucosyl derivatives **6** and **14** (Table 3), while mature plants contain the corresponding allosyl derivatives **8** and **16**, suggests that these allosides may be formed directly by epimerization at C-3″ of the glucosides. Likewise, **18** could be formed by reduction of **14**. Compound **10** from *M. involucrata* is found together with **6** but in this case several steps from **6** to **10** are necessary and no obvious pathway can be deduced.

In addition to the possibilities discussed above, alternative routes could lead to formation of the epoxydecaloside derivatives (see Scheme 1). Thus **6** could be formed either by glucosylation of **4** or by epoxidation of **14**; similar alternatives might be applicable for **8** and **10**. However, deutzioside (**1**) is usually found in the plants containing the epoxydecaloside derivatives (Table 3) and the most probable pathway in the formation of these compounds is thus via **1**.

The taxonomy of *Mentzelia* will be discussed elsewhere.

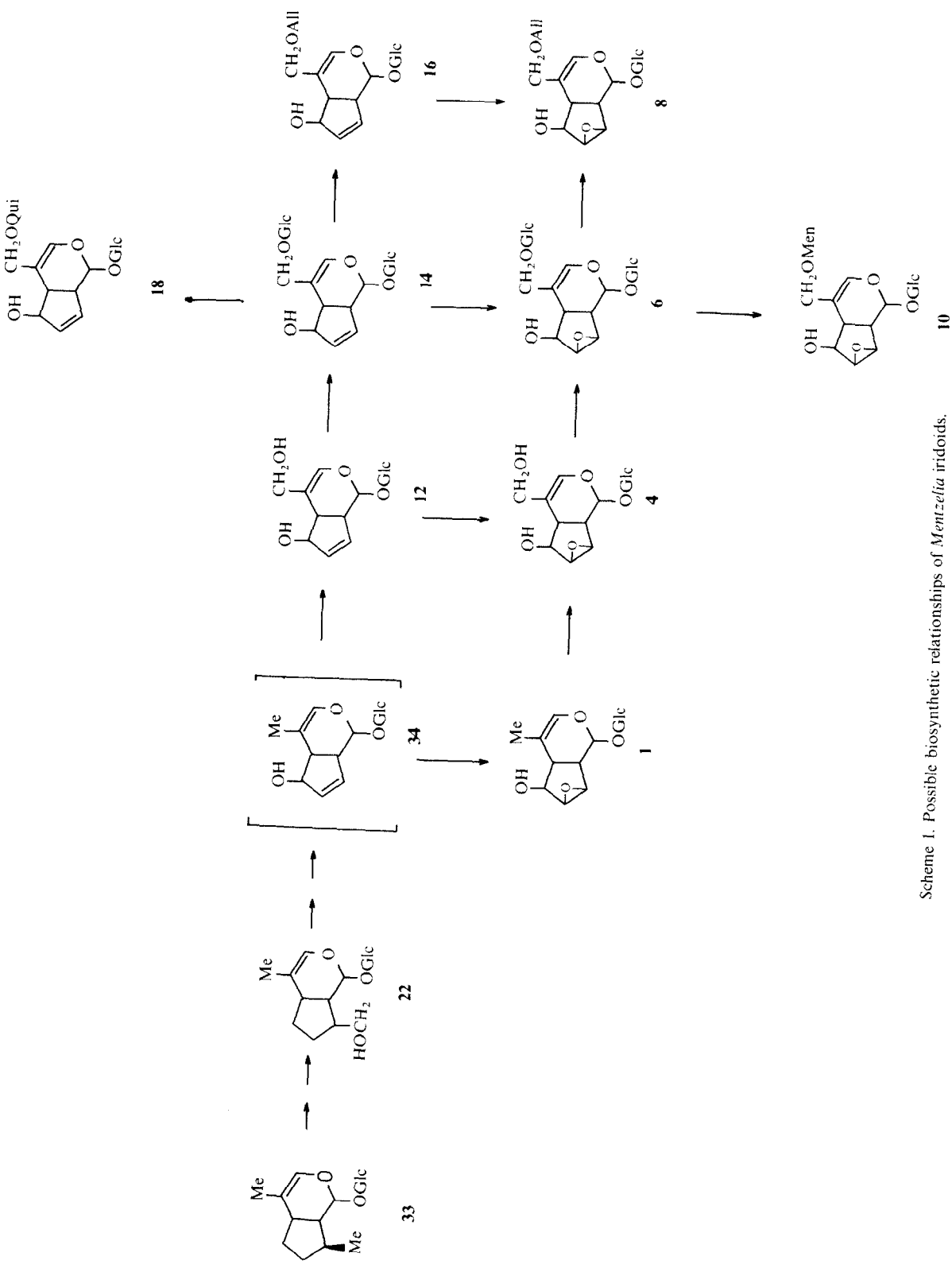
Table 3. Compounds isolated from *Mentzelia* species*

Species	Voucher†		1	3	4	6	8	10	12	14	16	18	20	Others
M. arborescens Urban & Gilg	HJT 3387	dry, ripe fol.											+	**32**: 0.06
M. albescens (Gill. ex Arn) Grisebach	HJT 3798	dry, ripe fol.					0.1		+		0.4		+	**32**: 0.04 **22**: +
		fresh,‡ young seedl. (10 cm)	0.005	0.001		0.003			0.045	0.02				**22**: 0.002
M. lindleyi Torr. & Gray	IOK 75/76	fresh,‡ flowering							0.1	0.05		0.05		**22**:0.02 **26**: 0.02
M. ravenii Thomps. & Roberts	HJT 3838	flowering				+			0.2		+		0.007	**25**: 0.2
M. micranta (Hooker & Arnott) Torr. & Gray	HJT 3819	dry, flowering							0.4	0.1			+	
M. lindheimerii Urban & Gilg.	HJT 3722	dry, flowering			0.02	0.2								
M. pachyrrhiza I.M.Johnston	HJT 3727	dry, flowering							0.15	0.18				**24**: 0.04 **25**:0.12
M. involucrata Watson	HJT 3813 HJT 3815	stems + leaves	0.58			0.11		0.34						
		roots						1.0						
		flowers	1.5			1.5								

* Numbers in the table are percentage of dry weight (+: present in trace amount).

† HJT vouchers were determined by Prof. H. J. Thompson and deposited in the herbarium of the University of California, Los Angeles. The IOK voucher was determined by Dr. K. Rahn and deposited at the Botanical Museum, Copenhagen, Denmark.

‡ Calculated as percentage of dry weight (= fr. wt.:5).



Scheme 1. Possible biosynthetic relationships of *Mentzelia* iridoids.

EXPERIMENTAL

General procedures were as earlier described [12]. Microanalyses were performed at NOVO Microanalytical Laboratory, Bagsværd, Denmark. Fresh plant material obtained from the Botanical Garden was frozen in polyethylene bags and kept at −23°. Material from Professor Thompson had been freshly dried and was kept at room temp. in the dark.

General isolation procedures. Frozen plant material was homogenized in EtOH, filtered and taken to dryness. Dry material was ground and extracted with MeOH in a Soxhlet apparatus, and the extract taken to dryness. The residues from either procedure were then partitioned between H_2O and Et_2O, and the aq. soln filtered through act. C/celite (1:1; 1 g of act. C/g of dry plant material). After washing with H_2O and 20% aq. EtOH to remove mono- and disaccharides, the glycosides were eluted with EtOH and taken to dryness to give 'crude glycosides'. The individual glycosides were isolated by CC on Si gel with $CHCl_3$–MeOH (10:1 to 2:1; solvent A) and/or BuOH–MeOH–H_2O (7:1:3; solvent B) as the eluants. Solvent A separated the less polar compounds, while solvent B was used for the more polar compounds. A few examples of separations are given below. The compounds are listed in the order of elution from the column.

Mentzelia albescens. Frozen immature plants (260 g) grown in January in a greenhouse gave 1.2 g of crude glycosides. CC on Si gel (130 g) with solvent A gave **3** (10 mg), **22** (20 mg), **1** (60 mg), **12** (310 mg), followed by a mixture of **12**, **14**, **6** and carbohydrates (600 mg). Rechromatography of the last fraction with solvent B gave **12** (290 mg), **14** (100 mg), **14** in admixture with carbohydrates (2:1, 150 mg), and a mixture of **6** and **14** (1:1, 85 mg).

M. pachyrrhiza. Dry plants (10 g) gave 80 mg of crude glycosides. Prep. TLC (solvent A) provided **24** (4 mg), **25** (12 mg), **12** (15 mg) and **14** (18 mg).

M. involucrata. Dry leaves and stems (190 g) gave 2.0 g crude glycosides. CC (solvent B) yielded **1** (1.1 g), **10** (640 mg) and a mixture of **6** and carbohydrates (2:1, 330 mg).

Identification of individual compounds. ^{13}C and ^1H NMR data are listed in Tables 1 and 2. Acetylations (pyridine, Ac_2O) were performed at room temp., and the products were chromatographed on Si gel with Et_2O as eluent.

Deutzioside (**1**) was crystallized from MeOH; mp 273–275° dec.; $[\alpha]_D^{22}$ −104° (*c* 0.3; H_2O). Lit. mp 266–270° dec.; $[\alpha]_D^{23}$ −101° (*c* 1.0; H_2O) [1], and 271–273.5° dec.; $[\alpha]_D^{17}$ −97° (*c* 0.5; H_2O) [6]. Acetylation gave **2**, mp (EtOH) 205°; $[\alpha]_D^{22}$ −108° (*c* 0.24; $CDCl_3$). Lit. mp 199°; $[\alpha]_D^{26}$ −103° (*c* 0.97; $CHCl_3$) [1] and mp 203.5–204° [6].

6′-O-Acetyl deutzioside (**3**) was crystallized from EtOH; mp 223–225° dec.; undepressed by admixture with a synthetic specimen. This was prepared from **1** (250 mg) in pyridine (4 ml) by reaction with Ac_2O (73 mg, 1 eqiv.). Work-up gave a mixture of **1** with several mono- and diacetates. CC (solvent A, 8:1) gave **3** (52 mg) mp 227° dec.; $[\alpha]_D^{22}$ −82° (*c* 0.34; MeOH). ^1H NMR: δ 4.33 (*m*, 6′-CH_2); 2.09 (*s*, OAc). (Found: C, 51.41; H, 6.40. $C_{17}H_{24}O_{10} \cdot 0.5\ H_2O$ requires: C, 51.38; H, 6.34%).

Epoxydecaloside (**4**) was isolated from *M. lindheimerii*. Mp (EtOH) 187–188° dec.; $[\alpha]_D^{22}$ −86° (*c* 0.27; MeOH). (Found: C, 44.51; H, 6.62. $C_{15}H_{22}O_{10} \cdot 2.5\ H_2O$ requires: C, 44.22; H, 6.68%). Acetylation gave **5**, mp (EtOH) 176°; $[\alpha]_D^{22}$ −115° (*c* 0.34; $CHCl_3$). (Found: C, 52.53; H, 5.66. $C_{27}H_{34}O_{16}$ requires: C, 52.77; H, 5.58%).

Glucosyl-epoxydecaloside (**6**) was isolated from *M. lindheimerii*. The compound was crystallized from 80% aq. EtOH, mp 216–217° dec.; $[\alpha]_D^{22}$ −87° (*c* 0.5; H_2O). The distinguishable ^1H NMR signals are recorded in Table 2; from the integrals it appeared that two glucose moieties were present. (Found: C, 46.48; H, 6.33. $C_{21}H_{32}O_{15} \cdot H_2O$ requires: C, 46.49; H, 6.31%). Acetylation gave **7**, mp 109–110°; $[\alpha]_D^{22}$ −81° (*c* 0.4; $CHCl_3$). (Found: C, 50.39; H, 5.73. $C_{39}H_{50}O_{24} \cdot 1.5\ H_2O$ requires: C, 50.37; H, 5.75%). The compound was hygroscopic.

Allosyl-epoxydecaloside (**8**) was isolated from *M. albescens*, mp (80% aq. EtOH) 274–275° dec.; $[\alpha]_D^{22}$ −98° (*c* 0.6; H_2O). Distinguishable ^1H NMR signal at δ 4.17 (*br. s*; H-3″). (Found: C, 47.36; H, 6.16. $C_{21}H_{32}O_{15} \cdot 0.5\ H_2O$ requires: C, 47.27; H, 6.22%). Acetylation gave **9**, mp 191–192°; $[\alpha]_D^{22}$ −77° (*c* 0.5; $CHCl_3$). ^1H NMR: δ 5.68 (*t*, J = 2.5 Hz; H-3″). (Found: C, 51.87; H, 5.57. $C_{39}H_{50}O_{24}$ requires: C, 51.88; H, 5.58%).

Mentzelosyl-epoxydecaloside (**10**) was isolated from *M. involucrata* (see above), mp (80% aq. EtOH) 236–237° dec. (H_2O of cryst. was lost at 165°); $[\alpha]_D^{22}$ −108° (*c* 0.4; H_2O). ^1H NMR (in addition to Table 2): δ 3.81 (*br. t*, J = 2 Hz, H-2″), 3.89 (*m*, $J_{2'',3''}$ = 2.5, $J_{3'',4ax''}$ = 8–12 Hz, H-3″), 1.77 (*m*, 4″-CH_2), 3.94 (*m*, $J_{5eq'',5ax''}$ = 12 Hz, H-5eq), 3.48 (*m*, H-5ax″). (Found: C, 46.46; H, 6.78. $C_{20}H_{30}O_{13} \cdot 2\ H_2O$ requires: 46.69; H, 6.66%). Acetylation gave **11**, mp 143–146° (hygroscopic); $[\alpha]_D^{22}$ −116° (*c* 0.6; $CHCl_3$). ^1H NMR: δ 5.20 (*m*, H-2″), 5.02 (*m*, H-3″), *ca* 2(*m*, 4″-CH_2), 4.03 (*dt*, $J_{5eq'',4''}$ = 4.5 Hz, H-5eq″), 3.45 (*m*, $J_{5ax'',4ax''}$ = 10 Hz, $J_{5ax'',4eq''}$ = 2.5 Hz, H-5ax″). (Found: C, 51.91; H, 5.58. $C_{34}H_{44}O_{20} \cdot H_2O$ requires: C, 51.65; H, 5.86%).

Decaloside (**12**) was isolated from several plants, mp (EtOH) 211–213°; $[\alpha]_D^{22}$ −141° (*c* 0.62; MeOH). Lit. [2]: mp 193°; $[\alpha]_D^{23}$ −138° (*c* 0.48; MeOH). Acetate **13**, mp 170–171°; $[\alpha]_D^{22}$ −140° (*c* 1.0; $CHCl_3$). Lit. [2]: mp 162–164°; $[\alpha]_D^{24}$ −128° (*c* 1.14; $CHCl_3$).

Glucosyl-decaloside (**14**) was not obtained in a pure state, and was characterized only by the NMR spectra (Tables 1 and 2). Acetylation gave crystalline **15**, mp 177–179°; $[\alpha]_D^{22}$ −126° (*c* 0.29; $CHCl_3$). (Found: C, 52.66; H, 5.64. $C_{39}H_{50}O_{23}$ requires: C, 52.82, H, 5.68%).

Allosyl-decaloside (**16**) was isolated from *M. albescens*, mp (80% aq. EtOH) 239° dec.; $[\alpha]_D^{22}$ −163° (*c* 0.54; H_2O). ^1H NMR: δ 4.15 (*br. s*; H-3″). (Found: C, 48.90; H, 6.31. $C_{21}H_{32}O_{14} \cdot 0.5\ H_2O$ requires: C, 48.74; H, 6.43%). Acetate (**17**), mp (EtOH) 145–146°; $[\alpha]_D^{22}$ −113° (*c* 0.50; $CHCl_3$); ^1H NMR: δ 5.7 (obscured by H-6, H-3″). (Found: C, 52.80; H, 5.59. $C_{39}H_{50}O_{23}$ requires: C, 52.82; H, 5.68%).

Quinovosyl-decaloside (**18**) was obtained from *M. lindleyi* in an impure state, and was characterized only by the NMR spectra. Acetate (**19**), mp (Et_2O) 156–157°; $[\alpha]_D^{22}$ −129° (*c* 0.70; $CHCl_3$); ^1H NMR: δ 1.31 (*d*, J = 6 Hz, 6″-Me). (Found: C, 53.26; H, 5.72. $C_{37}H_{48}O_{21}$ requires: C, 53.63; H, 5.83%).

Mentzetriol (**20**) was obtained in small amounts from several plants. Pooled fractions (125 mg) were rechromatographed on Sephadex G-15 (80% aq. MeOH) to give pure **20** (17 mg) as a syrup, $[\alpha]_D^{22}$ −345°, MS (50 eV; CI, isobutane) *m/e* (rel. int.): 153 ($M^+ + 1 - H_2O$, 54), 135 (95), 123 (87), 117 (43), 107 (48), 105 (100), 79 (40). This compound was not further characterized. Triacetate **21** was rather unstable and characterized only by the ^1H NMR spectrum (Table 2).

Mongolioside (**22**) was obtained as an impure syrup. ^1H NMR: δ 3.60 (*br. d*; $J_{8,10}$ = 7 Hz; 10-CH_2). Acetylation gave **23** with mp 114–115°. Mmp with an authentic sample obtained from *Viburnum mongolicum* [10] proved the identity. ^1H NMR: δ 4.05 (*br. d*; $J_{8,10}$ = 6 Hz, 10-CH_2).

Loganin (**24**) *and sweroside* (**25**) were identified by comparison (TLC, solvent A; ^1H NMR) with authentic samples.

Secoxyloganin (**26**) was isolated from *M. lindleyi*, but could not be purified completely, even by Sephadex (G-20) chromatography. ^1H NMR: δ 7.48 (*d*, $J_{3,5}$ = 1 Hz, H-3), 5.48 (*d*, $J_{1,9}$ = 6 Hz, H-1), 3.69 (*s*, OMe), 2.51 (*dd*, $J_{5,6}$ = 6 Hz, J_{6gem} = 8.5 Hz, H-6). CH_2N_2 (*ca* 0.5 mmol) in Et_2O was added to **26**

(35 mg), and excess destroyed after 2 min by adding HOAc. Evapn gave crude **27** (40 mg); ^{1}H NMR: δ 7.51 (*br. s*, H-3), 5.48 (*d*, $J_{1,9}$ = 5.5 Hz, H-1) 3.69 (*s*, OMe), 3.65 (*s*, OMe). Acetylation of **27** gave **28** (*ca* 20 mg), which was chromatographed (Et_2O) and crystallized. (EtOH); mp 144.5–145°, $[\alpha]_D^{18}$ −96° (*c* 0.2; $CHCl_3$). Lit. [32] mp 140.5°, $[\alpha]_D$ −99° ($CHCl_3$); and [11] mp 145°, $[\alpha]_D^{25}$ −107° ($CHCl_3$). ^{1}H NMR: δ 7.36 (*d*, $J_{3,5}$ = 2 Hz, H-3), 3.68 (*s*, OMe) 3.64 (*s*, OMe), 2.27 (*dd*, $J_{5,6}$ = 8, J_{6gem} = 16 Hz, H-6), 2.09–1.91 (4 × OAc), virtually as reported [11, 32].

Scopolin (**31**) from *M. albescens* was acetylated to give the tetraacetate, mp 158–162°; mmp 158–163° with an authentic sample.

Cleavage of **9** (73 mg) was performed in Et_2O (7 ml) and Ac_2O (1.5 ml) at room temp. by addition of $BF_3(Et_2O)_2$. After stirring for 30 min, ice and pyridine (3 ml) was added and stirring continued for 30 min. Work-up gave a mixture from which penta-*O*-acetyl-β-allopyranose (24 mg) was isolated by prep. TLC (Et_2O). The isolate had $[\alpha]_D^{22}$ −0.3° and could not be crystallized. However, the ^{1}H NMR spectrum was identical with an authentic spectrum.

Cleavage of **11** (223 mg) in Et_2O–Ac_2O (1:1; 5 ml) was achieved by adding $BF_3(Et_2O)_2$ (1 ml) with stirring at 0°. The mixture was allowed to warm to room temp. (*ca* 7 min) and again cooled; pyridine (5 ml), satd $NaHCO_3$ soln (5 ml) and ice were added, and stirring was continued for 15 min. Extraction with Et_2O and CH_2Cl_2 (50 ml each) gave 260 mg of a mixture which was separated by prep. TLC (Et_2O) to give as the faster moving band an anomeric mixture of tri-*O*-acetyl mentzelopyranoses (18 mg), $[\alpha]_D^{22}$ −5° (*c* 1.6; $CHCl_3$). ^{1}H NMR: δ 5.68 (*d*, *J* = 6.5 Hz), 5.95 (*d*, *J* = 3 Hz). The slower moving band (134 mg) consisted of **5**, identical to the preparation above.

*Tetra-O-benzoyl-2-deoxy-*D-erythro-*penitol* (*2-deoxy-*D-*ribitol-tetrabenzoate*). The mixture of mentzelose triacetates isolated from the cleavage of **11** (17 mg) was deacetylated (EtOH–NaOEt) for 30 min, then $NaBH_4$ (1 mg) was added under stirring and the mixture left overnight. Work-up followed by benzoylation (pyridine–BzCl) gave, after chromatography, the title compound (9 mg), mp 128–130°, $[\alpha]_D^{22}$ −15° (*c* 0.54; $CHCl_3$), identical to a sample prepared [33] from 2-deoxy-D-ribose.

Cleavage of **17** (*ca* 0.2 g) was performed using the same conditions as for **11**. Separation gave as the slowest moving band unreacted **17** (73 mg), followed by decaloside hexaacetate (**13**, 44 mg, identical with the sample above), and penta-*O*-acetyl-β-allopyranose (18 mg). The latter could not be crystallized; it had $[\alpha]_D^{22}$ −5° (*c* 0.2; $CHCl_3$). Further chromatography using EtOAc–hexane as the eluant gave no visible separation, but halving the band provided as the faster moving fraction pure penta-*O*-acetyl-β-D-allopyranose (6.5 mg), $[\alpha]_D^{18}$ −15° (*c* 0.7; $CHCl_3$) followed by the same compound contaminated with *ca* 15% of the α-anomer (7 mg), $[\alpha]_D^{18}$ +3° (*c* 0.7; $CHCl_3$). ^{1}H NMR: δ 5.98 (*d*, *J* = 9 Hz; H-1β), 6.32 (*d*, *J* = 3.5 Hz; H-1α). Penta-*O*-acetyl-α-D-allopyranose has not been reported in the literature, but estimating the difference in optical rotation between the anomeric acetates of allopyranose to be approximately the same as that for the corresponding glucopyranose derivatives (i.e. *ca* 100°) would explain the $[\alpha]_D$ of 0° for the preparation obtained by the cleavage of **9** (see above).

Cleavage of **19** (70 mg) as above gave unreacted **19** (24 mg) and **13** (15 mg) together with a mixture (1:4) of the α- and β-anomers of tetra-*O*-acetyl quinovopyranose (11 mg); ^{1}H NMR: δ 6.25 (*d*, *J* = 3.5 Hz, H-1α), 5.77 (*d*, *J* = 8 Hz, H-1β). Crystallization (Et_2O–pentane) gave tetra-*O*-acetyl β-D-quinovopyranose (2,5 mg), mp 142–144°, $[\alpha]_D^{19}$ +20° (*c* 0.2; $CHCl_3$). Lit. [34]: mp 144–145°, $[\alpha]_D$ +20.0° (*c* 2.2; $CHCl_3$).

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NOTE ADDED IN PROOF

5-*O*-β-glucosyl-macfadienoside (calycinoside) [35] also has two glycosyl moieties.