IRIDOID GLYCOSIDES FROM *MENTZELIA DECAPETALA*

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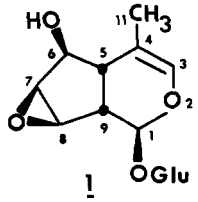
ABSTRACT.—A study of the iridoid glycosides of *Mentzelia decapetala* (Pursh.), Urban and Gilg, yielded five new compounds: 7-chlorodeutziol (**3**), loasaside (**10**), strictoside (**13**), decapetaloside (**12**), and 11-*O*-β-glucosyl decaloside (**14**), whose structures were elucidated by spectral and chemical means. In addition, three known iridoid glucosides were isolated: mentzeloside (deutzioside) (**1**), decaloside (**2**) and sweroside (**11**).

A preliminary study of an ethanolic extract of *Mentzelia decapetala* (Pursh.) Urban and Gilg. (Loasaceae) showed it to exhibit hypotensive activity. A phytochemical investigation yielded choline, which was the active principle, as well as the inactive constituents, scopoletin, rutin and eight iridoid glycosides (1). The iridoids (fig. 1) are the subject of this paper. Of these, mentzeloside



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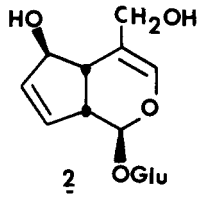

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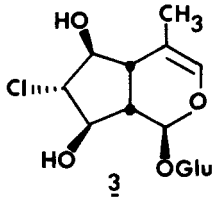

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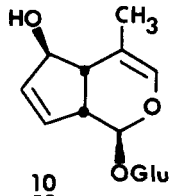

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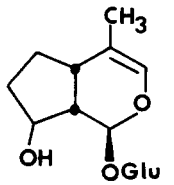

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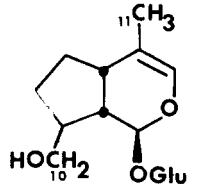

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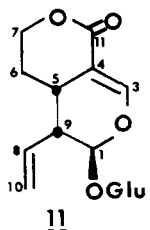

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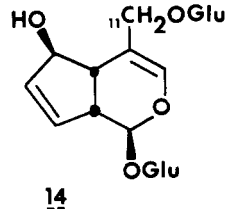

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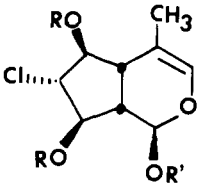
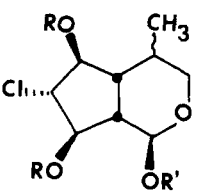
(deutzioside) (**1**), decaloside (**2**) and sweroside (**11**), are known compounds, with the first two previously reported from this source (2). The other five, 7-chlorodeutziol (**3**), loasaside (**10**), strictoside (**13**), decapetaloside (**12**), and 11-*O*-β-glucosyl decaloside (**14**), are new compounds.[1]





3 R=H ; R'=Glu
4 R=Ac ; R'=Glu(Ac)$_4$
5 R=R'=H
6 R=R'=Ac

7 R=H ; R'=Glu
8 R=Ac ; R'=Glu(Ac)$_4$
9 R=R'=H

RESULTS AND DISCUSSION

The ethanolic extract residue of the dried tops of *M. decapetala* was partitioned between chloroform and water, and the aqueous phase was extracted successively with ethyl acetate and *n*-butanol. The glycosides were isolated from the *n*-butanol and the final aqueous fraction by careful chromatography. The constituents are discussed individually as follows.

7-Chlorodeutziol (**3**), from the *n*-butanol solubles, is a white crystalline compound, mp 126–8°d, $[\alpha]_D -132°$ with composition $C_{15}H_{23}O_9Cl$ determined from elemental analyses. The ir spectrum showed absorption at 3400 (hydroxyl) and 1670 cm^{-1} (enol ether), and the uv spectrum displayed a λ max at 209 nm for an isolated double band. Acid hydrolysis yielded an unstable aglycone and glucose, identified by glc and tlc. The ^{1}H-nmr spectrum showed a broadened singlet at 6.10 ppm which was assigned to the enol ether proton at C–3, which is comparable to the value 6.13 ppm observed for mentzeloside (**1**) (2). The three-proton signal at 1.67 ppm indicated a C–4 olefinic methyl and the broad singlet at 2.34 ppm was assigned to the bridgehead protons at C–5 and C–9. The acetal protons of the aglycone and of glucose appeared as doublets at 5.36 ($J=1.6$ Hz) and 4.75 pp, ($J=7.6$ Hz), respectively. The ^{13}C-nmr spectrum showed peaks for 15 carbons (table 1). The assignments are based upon comparison of data for known iridoids (3) and results from undecoupled spectra.

Acetylation of 7-chlorodeutziol (**3**) to a hexaacetate **4** showed the aglycone portion to possess a diol, while hydrolysis with the β-glucosidase, emulsin, yielded the aglycone (**5**) and glucose. The aglycone triacetate **6** was assigned a structure from ^{1}H-nmr studies with the iridoid nucleus as a framework. Besides the expected peaks for an olefinic methyl, three acetates and an olefinic proton, a number of multiplets were present that were resolved by double irradiation experiments. Irradiation at 2.60 ppm (overlapping H–5 and H–9) converted the H–1 doublet at 6.17 ppm to a singlet and the overlapping multiplets at 5.42–

[1]The structures of these new compounds were presented at the International Research Congress on Medicinal Plant Research in Strasbourg, France, July, 1980. At the completion of this work, we received a personal communication from Dr. S. R. Jensen and Dr. B. J. Nielsen, Institute of Organic Chemistry, The Technical University of Denmark, in which they reported the isolation and identification of glucosyl decaloside, decapetaloside (which they named mongolioside), decaloside, mentzeloside and sweroside from another species of *Mentzelia*. This work has now been published: S. R. Jensen, C. B. Mikhelsen, and B. J. Nielsen, *Phytochemistry*, **20**, 71 (1981).

TABLE 1. ^{13}C-nmr of iridoids from *Mentzelia decapetala* (D_2O).

Carbon #	7-chlorodeutziol **3**	mentzeloside **1**	loasaside **10**	strictoside **13**	decapetaloside **12**	decaloside **2**	sweroside **11**
1	95.2	96.7	97.7	95.4	97.1	97.7	98.1
3	135.3	135.6	135.7	133.4	133.9	139.0	153.8
4	115.7	113.4	114.5	116.1	115.8	116.4	105.3
5	46.4	42.5	48.4	35.7	38.4	47.5	27.0
6	82.1	78.4	81.2	27.6	27.4	80.9	24.9
7	70.9	56.4	134.7	32.8	29.8	134.3	70.1
8	78.1	59.6	134.9	74.7	42.8	135.7	131.9
9	41.5	41.0	46.9	50.6	44.7	43.4	42.2
10	—	—	—	—	65.8	—	121.2
11	16.8	15.8	16.4	15.4	15.6	61.3	169.8
1'	100.3	99.8	99.3	99.1	97.1	99.1	98.8
2'	74.6	73.4	73.5	73.3	73.3	73.3	73.2
3'	77.6	76.9	77.0	76.7	76.7	76.7	76.8
4'	71.6	70.2	70.4	70.2	70.1	70.1	70.1
5'	77.3	76.4	76.5	76.3	76.2	76.3	76.1
6'	62.8	61.2	61.5	61.3	61.2	61.8	61.3

5.26 ppm to two doublets assigned to H–6 and H–8. That the remaining coupling of the latter protons was due to the proton (H–7) at 4.06 ppm was demonstrated when irradiation at about 5.35 ppm changed the double doublet pattern to a singlet. Reverse irradiation confirmed this relationship and requires that the chlorine be located at C–7.

Hydrogenation of 7-chlorodeutziol (**3**) gave a dihydro derivative **7** that lacked olefinic absorption in the ir spectrum and showed in the ^{1}H-nmr spectrum a three-proton doublet at 0.88 ppm ($J=6$ Hz) for the secondary methyl and loss of the olefinic proton at 6.10 ppm. 7-Chlorodihydrodeutziol (**7**) was converted to a hexaacetate **8** and hydrolyzed with emulsin to yield the crystalline aglycone **9**.

The spectral and chemical data for 7-chlorodeutziol (**3**) was consistent with a chlorohydrin structure derived from mentzeloside (deutzioside) (**1**). A chemical interconversion of the two substances was possible. Mentzeloside was produced from 7-chlorodeutziol by treatment with potassium carbonate and the reverse transformation was accomplished with methanolic hydrochloric acid. This established the complete stereochemical structure for 7-chlorodeutziol (**3**). That this compound could have been an artifact of isolation was ruled out by chromatographic examination of the crude ethanolic extract and by its isolation via a procedure devoid of chlorine-containing solvents. The literature records three other chloroiridoid glycosides, linarioside (4), eustoside (5) and valechlorine (6).

Mentzeloside (deutzioside) (**1**), isolated from the *n*-butanol-soluble fraction and its pentaacetate were identified by direct comparison with authentic samples.

Loasaside (**10**) was isolated from the *n*-butanol-soluble fraction, mp 216–20° and $[\alpha]_D-150°$. The ms showed a molecular ion peak at *m/e* 330 corresponding to $C_{15}H_{22}O_8$ and a strong peak at *m/e* 168 (M–162) which indicated the loss of a hexose. The ir spectrum showed absorption at 3400 (hydroxyl) and 1665 cm^{-1} (enol ether), and the uv spectrum showed a peak at 207 nm characteristic of an enol ether double bond lacking a β-carbonyl substituent.

The ^{13}C-nmr indicated the presence of fifteen carbons (table 1). The ^{1}H-nmr spectrum of **10** showed a broadened one-proton signal at 5.94 ppm assigned to the proton of an enol ether (C–3), a three-proton signal at 1.54 ppm for the methyl group at C–4, and a slightly broadened two-proton singlet at 5.86 ppm for two olefinic protons at C–6 and C–7. The methyl group was placed at C–4 instead of C–8 because it is coupled to H–3 and its chemical shift is similar to the C–4 methyls of 7-chlorodeutziol (1.67 ppm) and mentzeloside (1.61 ppm) rather than the C–8 methyl of linaride (1.88 ppm). A one-proton doublet at 4.93 ppm ($J=5.1$ Hz) was assigned to the acetal proton at C–1 of the aglycone.

The second olefinic function could be at carbon-6 or -7. In Δ^6-iridoids, H–6 appears at 6.1–6.3 ppm and H–7 at 5.6–5.7 ppm (3). For Δ^7-iridoids without a C–8 substituent, of which the only example is decaloside, a broad two-proton singlet at 5.83 ppm is observed, which is comparable to loasaside with absorption at 5.86 ppm.

Acetylation of loasaside yielded a highly unstable pentaacetate, and attempts at epoxidation of loasaside to mentzeloside were unsuccessful. However, correlation of mentzeloside with loasaside was achieved through a deoxygenation reaction with sodium iodide and zinc in acetate buffer (7). Both the Δ^6- and Δ^7-isomers were formed in low yield.

Loasaside (**10**) was also correlated with decaloside (**2**) through the following experiments: Partial hydrogenation of decaloside over Rh on C gave 7,8-dihydrodecaloside, which was hydrogenolyzed over Pd on C to a compound identical (tlc, ^{1}H-nmr) with the product (7,8-dihydroloasaside) of hydrogenation (Pd on C) of loasaside. Acetylation of 7,8-dihydroloasaside yielded a pentaacetate, which eliminated the possibility of hydrogenolysis of the allylic alcohol. Since decaloside and mentzeloside have an established stereochemistry at C–1, C–5, C–6 and C–7, we can conclude that loasaside is compound **10**.

Sweroside (**11**), a known compound, was isolated from the *n*-butanol-soluble fraction (8). Its identification was based on comparison of the mp and $[\alpha]_D$ of its acetate with the reported literature values and by direct comparison of the ^{1}H-nmr peaks of the free compound and the acetate with those of authentic reference samples. In addition, physical data for the hydrogenated product compared favorably with that reported for dihydrosweroside tetraacetate (8). The ^{13}C-nmr data for sweroside is presented in table 1.

Decapetaloside (**12**) was isolated from the *n*-butanol solubles as an oily residue. Glucose was identified as a product of both acid and emulsin hydrolysis, with the latter reaction indicating the presence of a β-glycosidic linkage.

The mass spectrum of **12** had a molecular ion peak at *m/e* 346 (1.4%), corresponding to formula of $C_{16}H_{26}O_8$, and base peak at *m/e* 184 (M^+-glucosyl). Acetylation of **12** produced a crystalline pentaacetate, $C_{26}H_{36}O_{13}$, with a molecular ion peak at *m/e* 556 (0.6%).

The ^{1}H-nmr spectrum of **12** contained a broad singlet at 5.90 ppm for H–3 of an enol ether system. Its chemical shift indicated no β-carbonyl substituent, and the lack of multiplicity supported a C–4 substituent. The three-proton peak at 1.36 ppm was assigned to a methyl group at C–4, as is present in mentzeloside, 7-chlorodeutziol, and loasaside. The glucosidic proton at C–1 appeared as a doublet centered at 4.99 ppm ($J = 4.1$ Hz). The ^{13}C-nmr data is given in table 1.

The aglycone contains one oxygen in addition to the ring oxygen. Assuming a normal iridoid skeleton, the location of the oxygen as a hydroxyl was placed at C–10, because: 1) the chemical shifts for the methyl in the ^{1}H-nmr (1.36 ppm) and ^{13}C-nmr (15.6 ppm) spectra are more in agreement with the values observed for those of mentzeloside (1.60, 15.8 ppm), 7-chlorodeutziol (1.67, 16.8 ppm) and loasaside (1.54, 15.4 ppm) with a C–4 methyl, than montinioside (1.18, 19.3 ppm) with a C–8 methyl; and 2) the position of the two allylic acetate protons would be expected at about 4.7 ppm as in the case of decaloside, whereas the saturated hydroxymethylene acetate protons would appear near 4.0 ppm as in adoxoside (4.06 ppm) (9) and patrinoside (4.05–4.20 ppm) (10). These protons appear at 3.98–4.20 ppm for decapetaloside pentaacetate.

The stereochemistry of the protons at C–5 and C–9 was assumed to be *cis* as is the case with all the known natural iridoid glucosides. Thus, the structure and stereochemistry of decapetaloside is established as **12** with the stereochemistry at C–8 yet to be determined.[2]

Strictoside (**13**) was isolated as an oily residue from the *n*-butanol solubles of

[2]The sterochemistry at C–8 should be β (see reference 17).

M. strictissima and *M. decapetala*. The presence of glucose was determined after acid hydrolysis through tlc and glc analysis of the TMS-derivative. Emulsin hydrolysis indicated a β-glycosidic linkage and produced an aglycone and glucose.

The ^{1}H-nmr spectrum showed the presence of a broad singlet at δ5.89 (1H) for H-3 of the enol ether system. Its chemical shift indicated no β-carbonyl substituent, and the lack of multiplicity supported at C-4 substituent. The presence of a signal at 1.38 ppm (3H) was assigned to a C-4 methyl, as already shown for the other iridoids of *Mentzelia*. The glucosidic proton at C-1 appeared as a doublet centered at 5.14 ppm ($J=3.5$ Hz). The ^{13}C-nmr data (table 1) indicated the presence of 15 carbons.

The ms spectrum of **13** showed a molecular ion peak at *m/e* 332 (0.5%), in agreement with a molecular formula of $C_{15}H_{24}O_8$, and a fragment at *m/e* 170 (43%) for the loss of a glycosyl unit. A crystalline pentacetate, $C_{25}H_{34}O_{13}$, (mp 149–150°) was prepared whose ir spectrum lacked adsorption for a free hydroxyl group. The ms spectrum showed a molecular ion peak at *m/e* 542 (0.72%) and a peak at *m/e* 331 for glucosyl tetracetate.

The presence of a hydroxy group on the aglycone was supported by the ^{13}C-nmr, as well as the formation of the pentaacetate, and could be located at C-6, C-7, or C-8 since C-5 and C-9 carry one proton each. Strictoside and 7,8-dihydroloasaside are chromatographically and spectroscopically different, therefore, a 6-β-hydroxy substitution is excluded. The emulsin-produced aglycone of strictoside, upon acetylation, afforded a diacetate whose examination by double-irradiation ^{1}H-nmr located the position of the hydroxyl.

Irradiation of the H-1 pattern at 6.18 ppm decoupled the pattern at 2.35 ppm thereby locating H-9. A similar irradiation of the proton on the acetate-bearing carbon at 5.00 ppm also caused alteration of the H-9 pattern. Thus the acetate and, in turn, the hydroxyl of strictoside (**13**) must be located at C-8. Additional decoupling studies allowed assignments to other protons.

Decaloside (**2**), a known iridoid glucoside, was isolated from both the *n*-butanol- and water-soluble fractions. Its identity was established by comparison of the physical and spectral data of both the free compound and the acetate derivative with the reported literature values (11).

11-O-β-Glucosyl decaloside (**14**) was obtained from the water-soluble fraction as a highly hygroscopic amorphous powder. Glucose was identified as the only sugar resulting from acid hydrolysis. The ^{1}H-nmr analysis of **14** indicated great similarity with that of decaloside. Strong signals in the ^{1}H-nmr region of 3.10–4.50 ppm plus the high polarity of the compound suggested the presence of more than one sugar moiety.

The location of the second glucosyl unit could be at either C-1, producing a glucosyl decaloside as in the case of genipin-1-*O*-β-gentiobioside (12), or at C-11 or C-6 as is the case of 5-*O*-β-glucosyl-antirrinoside (13) and melittoside (14) in which the two sugar moieties are on different carbons.

Acid methanolysis (14) of the tetrahydro derivative yielded, in addition to glucose, the monomethyl acetal which still retained one molecule of glucose. This confirmed that the two glucose units were not present as a disaccharide. Also, exhaustive methylation followed by hydrolysis (15) did not yield a trimethyl glucose, but only tetramethyl glucose as detected by glc analysis (12).

The nonaacetate of **14** showed in the ^{1}H-nmr spectrum a multiplet at δ5.63 consistent with an allylic acetate methine at C-6, as observed with decaloside, and thus eliminated the glucosyl unit from that position. Furthermore, the absence of two one-proton multiplets at 4.69 and 4.33 ppm for the protons of an acetylated primary alcohol at C-4 supported this position for the second glucose moiety.

Hydrogenation of **14** with Rh on C as catalyst produced the tetrahydro derivative; yet, under the same conditions, hydrogenation of decaloside (**2**) produced

the 7,8-dihydro derivative. Apparently the presence of a glycosyl unit at C-11 allows for reduction of the Δ^3-double bond. Acetylation of the tetrahydro derivative of **14** formed a nonaacetate, which established that hydrogenolysis had not taken place. Complete hydrolysis with emulsin of the tetrahydro derivative supported the β-glycosidic nature of the glucoside.

Based on the above information, the glycoside must be 11-*O*-β-glucosyl decaloside (**14**).

EXPERIMENTAL[3]

SOURCE OF PLANT MATERIAL.—*Mentzelia decapetala* (tops) was harvested from The Ohio State University College of Pharmacy Medicinal Plant Garden during the flowering state. The plant material was dried in a forced draft oven at 40° and powdered in a Wiley Mill.

EXTRACTION AND INITIAL PARTITION PROCEDURES.—Powdered plant material (1 kg) was extracted with 95% ethanol U.S.P. (~37 liters) at rt. The percolate was concentrated *in vacuo* to a semisolid residue (100 g) which was partitioned three times between two liters each of chloroform and water. The combined chloroformic extract on evaporation *in vacuo* gave 15 g of residue. The aqueous phase was extracted, successively, with three liters of ethyl acetate and *n*-butanol (each three times); after evaporation 4 g of ethyl acetate solubles and 16 g of *n*-butanol solubles were obtained. The aqueous phase, on evaporation, yielded 59 g of residue.

CHROMATOGRAPHIC STUDIES OF THE N-BUTANOL AND WATER SOLUBLES.—The three analytical systems of thin layer chromatography, paper chromatography, and gas liquid chromatography were used in this study.

Thin layer chromatography was performed on silica gel G (Merck) plates of 0.2 mm thickness with the following solvent systems and *p*-anisaldehyde-sulfuric acid as spray reagent.

Solvent System-I: chloroform-methanol-water (60:15:4) (lower phase)
Solvent System -II: *n*-butanol saturated with water (upper phase)
Solvent System-III: chloroform-methanol (3:1)

Ascending paper chromatography was performed on Whatman No. 1 3MM and vanillin hydrochloric acid in methanol as spray reagent with the following solvent systems:

Solvent System IV: *n*-butanol-acetic acid-water (63:10:27)
Solvent System V: *n*-butanol saturated with water

Gas liquid chromatography was performed with helium as the carrier gas (51 ml/min) at 250° on a 1.5 m 3% OV-17 column. Samples (1 mg) were trimethylsilylated by mixing with 0.5 ml of a reagent mixture composed of anhydrous pyridine (10 ml), hexamethyldisilizane (2 ml) and trimethylchlorosilane (1 ml) and warming in a stoppered vial at 40° for 15 min. A 2–5 μl aliquot was injected into the gas chromatograph.

The *n*-butanol-soluble fraction in 8.6 g portions was separated on a 100 g Sephadex LH-20 column (3 cm id x 65 cm) with methanol as eluent. Fractions of 7.5 ml were collected. Fractions 1–20 (19.3 g) contained nonflavonoid material, fractions 21–30 contained flavonoid material which crystallized from methanol (0.4 g) or methanol-water and was identified as rutin on the basis of comparison of its physical data (mp, optical rotation, ir, uv, ^{1}H-nmr) with that of an authentic sample.

COLUMN CHROMATOGRAPHY OF THE NONPHENOLIC PART OF THE *n*-BUTANOL-SOLUBLE FRACTION.—The nonphenolic material obtained from the Sephadex LH-20 column (19.3 g) was adsorbed on 25 g of silica gel #1 and applied to the top of a silica gel 60 column (1 kg. Merck, particle size 60–100 mesh, deactivated with 5% water; 6.5 cm id x 60 cm) and eluted with solvent system I. Fractions of 54 ml were collected after an initial 800 ml hold-up volume was collected. The fractions were combined according to tlc analysis (solvent system I) and the dry weight profile.

ACID HYDROLYSIS OF THE ISOLATED GLYCOSIDES.—The glycoside (5 mg) was dissolved in one ml of 0.5N sulfuric acid, and the reaction mixture was boiled at 95° for 90 min. Calcium

[3]Melting points are uncorrected and were determined on a Thomas-Hoover Unimelt Apparatus. Infrared spectra were determined on a Beckman model 4230 Infrared Spectrometer in chloroform or KBr pellet. Ultraviolet spectra were determined in methanol on a Beckman model 5260 Ultraviolet and Visible Spectrometer. ^{1}H-nmr spectra were determined in the stated solvents with either tetramethylsilane (TMS) as internal standard or sodium 3(trimethylsilyl)propane-sulfonate (DDS) as external standard on a Varian A-60A (60 MHz) instrument or a Bruker-HX90 (90 MHz) instrument equipped for pulse mode with Fourier transform analysis. ^{13}C-nmr spectra were taken on a Bruker-WP80 instrument at 20.1 MHz. Chemical shifts are reported in ppm (δ) and coupling constants in Hz. Dioxane was used as the external standard. Mass spectra were measured on an AEI MS-9 Mass Spectrometer, an Hewlett-Packard 5985 GC-MS (DIP) system and a Du Pont model 21-491 instrument. Gas chromatograms were obtained on a Hewlett-Packard Apparatus Model 5710A, equipped with a flame ionization detector. Optical rotations were measured on a Perkin-Elmer 241 Photoelectric Polarimeter. All reagents were analytical grade and solvents were redistilled. Silica gel G and silicic acid were from E. Merck (Darmstadt, Germany) and Mallinkrodt, (St. Louis, Mo.), respectively. Silica gel was sedimented in particle ranges 1 through 6 according to Pitra and Sterba (16).

hydroxide (20 mg) was then added. The reaction mixture was trimethylsilylated (as stated above) and a 2.5 μl aliquot was injected into the gc (oven temperature 180°).

The hydrolysis products presented two peaks with retention times of 5.8 min. and 7.8 min., which were identical with the peaks of authentic β-D-glucose and α-D-glucose.

EMULSIN HYDROLYSIS OF THE ISOLATED GLYCOSIDES.—The compound was dissolved in distilled water, and emulsin (Nutritional Biochemical Corp.) was added. The reaction mixture was kept at ambient temperature and was monitored by tlc until no more starting material was present. The reaction mixture was evaporated to dryness and extracted with a hot mixture of chloroform-methanol (1:1). The extract residue was purified by column chromatography. The aqueous phase retained the free sugar, which was identified as glucose by tlc and gc analysis.

ACETYLATION CONDITIONS.—Excess pyridine-acetic anhydride (1:1) was used at ambient temperature or at steam bath temperature. The reaction was monitored by tlc and continued until the starting material was gone. After work-up an attempt was made to crystallize the material, and, when necessary, chromatographic purification was carried out.

PURIFICATION OF 7-CHLORODEUTZIOL (3).—Fractions 256–278 (2.75 g) from the nonphenolic, *n*-butanol solubles were dissolved in methanol, adsorbed on 2 g of silica gel #1, and applied to the top of a column of Florisil (51 g, 60–100 mesh, J. T. Baker; 2 cm id x 42 cm). Elution was with the following solvents: chloroform-methanol 9:1 (3.6 liters), 85:15 (0.5 liter), 8:2 (0.5 liter), 75:25 (0.5 liter), and 7:3 (0.5 liter). Fractions of 9 ml were collected. Fractions 30–80 contained 7-chlorodeutziol (932 mg), which crystallized as colorless needles from methanol-chloroform (1:9). It gave the following physical and spectral properties: mp 126–8° with decomposition; $[\alpha]^{22}D-132°$ (c 1.0, H_2O), $[\alpha]^{20}D-132°$ (c 2.2, MeOH); uv (MeOH) λmax 209 (log ϵ 3.50); ir (KBr) νmax: 3400, 1620, 1670, 1090, 890 cm^{-1}; ^{1}H-nmr (90 MHz, D_2O, δ (ppm) 1.67 (s, 3H, Me at C-4), 2.34 (brs, 2H, H-5 and H-9), 3.47 (brs, sugar protons), 3.97 (m, H-6 and H-8), 4.75 (d, *J* 7.6 Hz, H-1'), 5.36 (d, *J* 1.6 Hz, H-1), 6.10 (s, H-3); ^{13}C-nmr (see table 1).

Analysis: Calcd for $C_{15}H_{23}O_9$ Cl.H_2O: C, 44.95; H, 6.29; Cl, 8.85. Found: C, 44.73; H, 6.24; Cl, 8.88%.

7-CHLORODEUTZIOL HEXAACETATE (4).—The hexaacetate 4 exhibited the following properties: mp 124–5° (MeOH); $[\alpha]^{20}D-125°$ (c 2.6, $CHCl_3$); Rf 0.24 (benzene-ethyl acetate, 3:1); ir ($CHCl_3$) no OH absorption and νmax at 1760 cm^{-1} (acetate); ^{1}H-nmr (90 MHz, $CDCl_3$) δ1.92–2.12 (s, 18H, 6 Ac), 1.65 (s, 3H, Me at C-4), 2.62–2.71 (br. s., 2H, H-5 and H-9), 3.77 (m, H's of sugar), 4.30–4.00 (m, H-6), 5.20–4.80 (protons base of acetate), 5.31 (br. s., H-1), 6.03 (s, H-3). The ^{13}C-nmr is presented in table 2.

Anal. Calcd for $C_{27}H_{35}O_{15}Cl$: C, 51.10; H, 5.52. Found: C, 50.91; H, 5.59%.

TABLE 2. ^{13}C-nmr of iridoid-acetates from *Mentzella decapetala* ($CDCl_3$)*.

Carbon #	7-chlorodeutziol (Acx6)	mentzeloside (Acx5)	lossaside (Acx5)	strictoside (Acx5)	decapetaloside (Acx5)	decaloside (Acx6)	sweroside (Acx4)
1	91.1	97.8	94.8	93.0	94.3	96.8	96.6
3	135.3	136.5	136.8	134.5	134.0	141.5	151.3
4	108.8	111.0	111.3	112.4	112.0	110.9	105.5
5	45.3	41.9	47.9	35.1	38.6	46.9	27.5
6	80.3	80.1	82.1	26.4	26.9	82.3	24.7
7	64.2	55.4	135.0	30.4	28.2	135.6	68.2
8	80.3	55.3	131.6	76.5	37.2	132.2	131.2
9	40.3	38.0	42.9	49.1	45.5	40.8	42.1
10	—	—	—	—	67.8	—	121.0
11	15.6	16.5	16.6	15.6	15.6	64.0	165.0
1'	95.6	96.0	96.1	95.8	95.9	96.8	96.0
2'	70.6	70.9	71.0	71.1	71.1	70.9	70.6
3'	72.1	72.8	72.9	72.9	72.8	72.8	72.3
4'	68.2	68.4	68.6	68.8	68.7	68.4	68.2
5'	72.5	72.2	72.2	72.2	72.7	72.2	72.3
6'	61.7	61.9	62.1	62.0	62.1	61.9	61.8

*Additional signals for the Acetate units are present.

AGLYCONE OF 3.—The aglycone 5 had the following peaks: ^{1}H-nmr (90 MHz, CD_3OD) δ1.65 (s, 3H, Me at C-4), 2.37–2.22 (m, 2H, H-5 and H-9), 3.80 (broad singlet, 3H, H-6, H-7, and H-8), 5.04 (d, *J* 3.6 Hz, H-1, and 6.00 (s, 1H, H-3); ^{13}C-nmr (acetone d_6) δ90.6 (C-1) 134.4 (3), 110.4 (4), 46.7 (5), 80.7 (6), 70.6 (7), 76.5 (8), 40.6 (9), and 14.6 (11).

7-CHLORODEUTZIOL AGLYCONE (5) TRIACETATE.—The acetate 6 exhibited the following properties: Rf 0.16 in chloroform and 0.63 in benzene-ethyl acetate (3:1); ir νmax ($CDCl_3$), 1750 cm^{-1} and no free OH; ^{1}H-nmr ($CDCl_3$): δ1.70 (s, 3H, Me at C-4), 2.09 (s, 3H, Ac), 2.13 (s, 6H, 2Ac), 2.70–2.60 (m, 2H, H-5 and H-9), 4.06 (m, H-7), 5.42–5.26 (m, 2H, H-6 and H-8), 6.10 (br. s., H-3), 6.17 (br. s., H-1). ^{13}C-nmr ($CDCl_3$) δ88.1 (C-1), 136.4 (3), 108.0 (4), 44.6 (5),

80.8 (6), 64.1 (7), 80.2 (8), 40.4 (9), 15.0 (11), 169.4 (3 carbonyl carbons) 21.0 (3 methyl-acetate carbons). The ms had a *m/e* at 286 (4.2%) (M-AcOH) with an (M-AcOH+2) peak at 288 (1.4%).

HYDROGENATION OF 3.—Activated palladium on charcoal (25 mg, 10%) was suspended in 10 ml of methanol and saturated with hydrogen for a 3 hour period, then a solution of 3 (121 mg) in 0.5 ml of water and 0.5 ml of methanol was added and the reaction maintained under a hydrogen atmosphere for five hours. The hydrogenated product 7 crystallized from methanol-chloroform (1:9) as aggregates of microneedles. It had a mp 128–131° dec; Rf of 0.05 in solvent system I, $[\alpha]^{23}D$ −88° (c 1.0, H_2O); ^1H-nmr (CD_3OD, 90 MHz) δ0.88 (d, *J* 6 Hz, 3H, Me at C-4), 1.30–2.24 (complex m, H-5, H-9 and H-4), 4.22–3.22 (protons base of hydroxyl groups), 4.55 (d, *J* 7.3 Hz, H-1') and 5.26 (s, H-1).

3,4-DIHYDRO-7-CHLORODEUTZIOL (7) HEXAACETATE.—Acetylated compound 8 crystallized from water as microneedles (6.9 mg) and had the following properties: mp 191–3°; Rf 0.22 (benzene-ethyl acetate, 3:1); ir νmax ($CHCl_3$) at 1755 cm^{-1} and no band for a free OH; ^1H-nmr ($CDCl_3$, 90 MHz) δ0.92 (d, *J* 5.7, Me at C-4), 2.02–2.13 (6 s, 18H, 6Ac), 3.12–3.62 (m, 2H-3 and H-7), 4.00–4.42 (m, sugar protons); 5.24–4.77 (protons base of acetates), 5.55 (d, *J* 6.0 Hz, H-1'), 5.67 (d, *J* 6.4 Hz, H-1). A Beilstein's test for chlorine was positive.

EMULSIN-DERIVED AGLYCONE OF 3,4-DIHYDRO-7-CHLORODEUTZIOL (7).—The crystalline aglycone 9 had the following properties: Rf of 0.39 (solvent system I); mp 114°) dec; uv (CH_3OH) end absorption; ^1H-nmr (Pyr-d_5, 90 Mz) δ0.90 (d, *J* 6.4 Hz, Me at C-4), 1.80 (m, H-4), 2.38–2.56 (dd, H-5), 2.89–3.07 (dd, H-9), 3.52–3.69 (dd, H-3a), 3.89–4.13 (dd, H-3b), 4.47–4.92 (complex signal, 3H, H-6, H-7 and H-8), 5.91 (br. s., H-1); ^{13}C-nmr (Pyr-d_5) at δ91.8 (C-1), 63.7t (3), 30.8d (4), 40.8d (5), 82.3d (6) 75.1d (7), 79.7d (8), 47.0d (9), and 15.8q (11). The mass spectrum presented a molecular ion peak at *m/e* 222 (2%).

SYNTHESIS OF MENTZELOSIDE FROM 7-CHLORODEUTZIOL.—7-Chlorodeutziol (50 mg) was reacted with anhydrous potassium carbonate (210 mg) in methanol (20 ml) for 17 hr at 25°. The reaction mixture was concentrated *in vacuo* and chromatographed on silica gel #4 (5g, 1cm id 5 cm) with solvent I as eluent. Fractions of 1 ml were collected. Fractions 61–80 (23 mg) were crystallized from methanol to yield 11 mg of mentzeloside, which was identified by its mp, mixture mp, ir and ^1H-nmr in comparison with a reference sample.

CONVERSION OF MENTZELOSIDE TO 7-CHLORODEUTZIOL.—Mentzeloside (7 mg) was dissolved in 5 ml of methanol to which 1 ml of a 0.02 N solution of HCl was added. The mixture was stirred for four days at room temperature. Partial transformation of mentzeloside into 7-chlorodeutziol occurred, as indicated by tlc and co-tlc.

EXTRACTION OF 7-CHLORODEUTZIOL WITH A NONHALOGENATED SOLVENT SYSTEM.—An ethanolic extract (11.2 g) of *M. decapetala* tops was partitioned between 50 ml each of ethyl ether and water. The aqueous portion was successively extracted with equal portions of ethyl acetate and *n*-butanol. The *n*-butanol-soluble fraction (1.2 g) was chromatographed on Florisil (52 g, 60–100 mesh, 25 cm id x 34 cm) with benzene-methanol (3:1) as eluent. Fractions of 15 ml were collected. 7-Chlorodeutziol was present in fractions 2–7 as indicated by tlc and paper chromatography.

ISOLATION AND IDENTIFICATION OF MENTZELOSIDE (1).—Results of tlc analysis indicated mentzeloside (1) to be present in fractions 219–255 of the chromatography of the *n*-butanol-soluble nonphenolic fraction. It was purified by chromatography of the crude material (850 mg) through a column of Florisil (51 g, 60–100 mesh, 2 cm id x 42 cm) and elution with increasing proportions of methanol in chloroform, 15 ml fractions were collected. Mentzeloside was obtained as crystalline material from fractions 130–140. It possessed the following properties: mp 260° (dec), $[\alpha]^{23}D$ −100° (c 1.0, H_2O), [Lit. mp 266°, $[\alpha]^{25}D$ −100.88° (c 1.02, H_2O) (2)]; ^1H-nmr (D_2O, 90 MHz) δ1.60 (s, 3H, Me at C-4), 2.70, 2.10 (2t, H-5 and H-9) 3.90–3.50 (m, H on oxygenated carbons), 4.15 (d, *J* 7.6 Hz, H-1'), 4.85 (d, *J* 10 Hz, H-1), 6.24 (brs, H-3); ^{13}C-nmr (D_2O) in table 1.

MENTZELOSIDE PENTAACETATE.—The pentaacetate had the following properties: mp 201° ($MeOH-H_2O$) [Lit. mp 199° (2)]; ir indicated no free hydroxyl, νmax 1760 (acetate) 1620 cm^{-1} (enol ether); tlc Rf of 0.5 (benzene-ethyl acetate, 3:1); ^1H-nmr ($CDCl_3$, 90 MHz) δ1.46 (s, Me at C-4), 2.30 (m, 1H, H-5), 2.50 (m, 1H, H-9), 3.56 (m, H-7, H-8 and H-5'), 4.80–4.10 (proton base of acetates), 6.00 (brs, 1H, H-3), and five acetates present at 2.07, 2.03, 1.99, 1.96 and 1.94; ^{13}C-nmr ($CDCl_3$) in table 2.

PURIFICATION AND PROPERTIES OF LOASASIDE (10).—Fractions 165–217 (1.4 g) from the *n*-butanol nonphenolic column separation contained a compound which gave, on tlc, a pink color which rapidly faded to a yellow-brown color. Purification of this fraction was achieved by column chromatography on Florisil (51 g) with chloroform-methanol (9:1) as eluant, 15 ml fractions were collected. Tubes 41–122 contained loasaside (446 mg), which was further purified on silica gel 60 (45 g) with solvent system I as eluant. Subfractions 71–190 (311 mg) were then passed through a silica gel #4 column (75 mg) with solvent system I again as eluent. Tubes 47–63 contained crystalline loasaside (150 mg), which, when recrystallized from methanol-chloroform (1:9), formed tiny needles.

Loasaside exhibited the following properties: it turned pink at 193° and melted with decomposition at 216–220°; $[\alpha]^{23}D$ −150° (c 1.3, H_2O), uv (CH_3OH), νmax, 207 nm (log ε 3.55); ir (KBr)

νmax 3400, 1665, 1620, 1350, 1380, 1150, 1100, 1045, 1010, 975, 965, 840, 800 cm^{-1}; ms had a molecular ion peak at 330 (0.6%); ^{1}H-nmr (D_2O, 90 MHz) δ1.54 (brs, 3H, Me at C-4) 2.42–2.38 (dd, 2H, H-5 and H-9), 3.57 (protons base of hydroxyl groups, sugar moiety), 4.93 (d, *J* 5.1 Hz, H-1), 5.86 (brs, 2H, H-7 and H-8), and 5.94 (brs, H-3); the ^{13}C-nmr (D_2O) is given in table 1.

LOASASIDE PENTAACETATE.—The pentaacetate had the following properties: mp 153–6°; (MeOH) tlc Rf 0.41 with benzene-ethyl acetate (3:1); highly unstable and turned yellow upon exposure to light; ir ($CHCl_3$) had no signals for free hydroxyl groups and νmax at 1750, 1600, 1370, 1050 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 90 MHz) δ1.66 (brs, Me at C-4), five acetates at 2.10, 2.06, 2.03, 2.01 (x2), 5.90–6.03 (dd, 3H, H-7 and H-8, and a broad singlet for H-3), 5.53 (m. H-6), 4.87–5.44 (signals for the proton base of acetates and glucosidic protons). The ^{13}C-nmr ($CDCl_3$) is presented in table 2.

HYDROGENATION OF LOASASIDE.—Activated palladium on charcoal (4.4 mg, 10%) was suspended in 1.5 ml of methanol and saturated with hydrogen for a two-hour period, then a solution of loasaside (10 mg) in 0.4 ml of methanol was added and the reaction maintained under a hydrogen atmosphere for 90 min. The 7,8-dihydroloasaside obtained had a Rf 0.23 (solvent system I) and the ^{1}H-nmr (D_2O, 90 MHz) indicated the absence of the signal at δ5.86 (2H), but present were δ6.04 (brs, 1H, H-3), 5.23 (d, *J* 2.5 Hz, H-1), 3.70–4.40 (protons base of hydroxy groups), 2.45 (brs, 2H, H-5 and H-9), 1.57 (s, 3H, Me at C-4), 1.00–1.90 (brm, 2H-7 and 2H-8).

ACETYLATION OF 7,8-DIHYDROLOASASIDE.—The dihydropentaacetate was obtained as an oil, ^{1}H-nmr ($CDCl_3$) δ2.02, 1.95 (x2), 1.94 and 1.90 (5 Ac), 5.87 (brs, H-3), 5.14–4.63 (complex pattern of protons base of acetates, plus glucosidic protons), 4.15 (m, H-6), 3.59–3.70 (protons of the sugar moiety), 2.44 (brs, 2H, H-5 and H-9), and 1.48 (brs, 3H, Me at H-4).

DEOXYGENATION OF MENTZELOSIDE AND FORMATION OF LOASASIDE AND OF Δ^6-ISOLOASASIDE.—Sodium iodide (210 mg) and sodium acetate (70 mg) were dissolved in 4.1 ml of glacial acetic acid containing 0.3 ml of water and cooled in ice. Activated zinc powder (300 mg) was added followed by mentzeloside (105 mg) over a period of ten minutes. The reaction mixture was stirred in an ice bath under nitrogen for one hour, filtered, diluted with water and concentrated under high vacuum. The residue was dissolved in 4 ml of water and 1 ml of glacial acetic acid, stirred and maintained under nitrogen in an ice bath for one hour. The reaction mixture was filtered through one gram of activated charcoal, washed with 40 ml each of water and methanol. Concentration of the methanol filtrate *in vacuo* produced a residue (83 mg) which was chromatographed on silica gel 60 with solvent system I as eluent; 2 ml fractions were collected. Fractions 26–40 contained 5 mg of Δ^6-isoloasaside with ^{1}H-nmr δ (D_2O, 90 MHz) 6.08 and 5.68 (2dd, 2H-6 and H-7, respectively), 5.88 (brs, H-3), 5.13 (d, *J* 3.8, H-1), 3.10–3.72 (protons base of hydroxyl groups), 2.25 (m, 2H, H-5 and H-9), and 1.43 (s, 3H, Me at C-4). Fractions 41–42 (32 mg) contained loasaside and mentzeloside. Additional chromatography of these fractions led to the isolation of 2.6 mg of pure loasaside, which was identified by its ^{1}H-nmr, tlc, co-tlc, and paper chromatographic analysis.

HYDROGENOLYSIS OF 7,8-DIHYDRODECALOSIDE.—Palladium on charcoal (17 mg, 10%), and 7,8-dihydrodecaloside (20 mg) was suspended in 2.5 ml of absolute ethanol, and the stirred solution was left under a hydrogen atmosphere at 21° for five hours. The reaction mixture was filtered and concentrated *under vacuo*. The residue (17 mg) was passed through a silica gel 60 column with solvent system I as eluent; 0.5 ml fractions were collected. From fractions 70–100, was obtained a compound (5 mg) which exhibited a single spot upon tlc analysis. It had Rf 0.23 with solvent system-I on silica gel, and its ^{1}H-nmr (D_2O) was superimposable with that of 7,8-dihydroloasaside.

Isolation of sweroside (**11**) *and decapetaloside* (**12**).—The residue of the combined fractions 89–103 (1 g) of the column chromatography of the nonphenolic *n*-butanol solubles was adsorbed on 3 g of silica gel #1 and applied to the top of a Florisil column (51 g, 100–200 mesh), then eluted with 0.5 liter of chloroform and 2.5 liters of chloroform-methanol (9:1) as eluent; 45 ml fractions were collected. Fractions 18–32 (0.5 g) with two components were separated by thick layer chromatography (silica gel as adsorbent and *n*-butanol saturated with water as eluent). The zone with Rf 0.65 yielded 85 mg of decapetaloside; the zone with Rf 0.55 yielded 95 mg of sweroside. *Sweroside* (**11**) was obtained as an oily residue, with ^{1}H-nmr (D_2O) δ (ppm) 1.65 (m, 2H-6), 2.67 (m, 2H, H-5, H-9), 3.20–4.20 (protons base of hydroxyl and 2H-7), 5.18–5.32 (m, 3H, H-8 and 2H-10), 5.40 (d, *J* 1.9 Hz, H-1), 7.47 (d, *J* 2.2 Hz, H-3). The ^{13}C-nmr (D_2O) is given in table 1.

Sweroside (**11**) *tetraacetate*.—The tetraacetate gave the following data: mp 165° (EtOH); Rf 0.29 (benzene-ethyl acetate, 3:1); $[\alpha]^{25}D$ −166° (c 4.3, $CHCl_3$); uv λmax ($CHCl_3$), 243 nm (log ε 3.69); ir ($CHCl_3$) νmax: 1760, 1720, 1620, 990 and 903 cm^{-1}; ^{1}H-nmr ($CDCl_3$) 1.97, 2.00, 2.03, 2.09 (4 Ac), 7.56 (d, *J* 2.5 Hz, H-3), 5.45–5.20 (m, H-8 and 2H-10). The ^{13}C-nmr ($CDCl_3$) is given in table 2. All of these data are in agreement with reported literature values for sweroside tetraacetate (17).

Hydrogenation of sweroside (**11**) *tetraacetate*.—The product crystallized from chloroform-ethanol as microneedles which had the following physical and spectral data: mp 183–5°; $[\alpha]^{24}D$ −144.5° (c 4.0 $CHCl_3$); uv ($CHCl_3$) λmax, 244 nm (log ε 2.9); ir ($CHCl_3$) νmax 1760, 1710, 1620, 1230, 1070, 1040 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ7.44 (d, *J* 2.5, H-3), 5.36 (d, *J* 1.5 Hz, H-1), 4.85–5.18 (proton base of acetate), 4.11–4.37 (m, 2H, H-7), 3.73 (m, sugar residue), 2.77 (m, 2H, H-5 and H-9), 2.03, 1.97, 1.94 and 1.89 (4 Ac), 0.90–1.00 (a complex adsorption with a deformed

triplet, 5H, H's-C-8 and C-10). [Lit. mp 180–1°, $[\alpha]^{29}D$ −108°, other values are in agreement with those reported in the literature (8)].

DECAPETALOSIDE (**12**).—Isolated as an oily residue, it exhibited the following spectral data: ^{1}H-nmr (D_2O) δ1.00–1.90 (m, 2H-6 and 2H-7), 1.36 (s, 3H, Me at C-4), 2.35 (m, 2H, H-5 and H-9), 3.20–3.70 sugar protons and 2H-10), 5.00 (d, *J* 4.1 Hz, H-1), 5.91 (brs, H-3); ms presented a molecular ion peak at 346 (1.4%). The ^{13}C-nmr (D_2O) is given in table 1.

DECAPETALOSIDE (**12**) PENTAACETATE.—The pentaacetate showed the following physical and spectral data: mp 114–5° (EtOH); $[\alpha]^{21}D$ −90° (c 3.7, $CHCl_3$); ir ($CHCl_3$) no free hydroxyl signal νmax at 1760–1740 (acetate), 1370, 1230, 1040, 990, 910 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ2.08, 2.05, 2.03, 2.01, 1.98 (5 acetates), 5.94 (brs, H-3), 4.90–5.25 (m, protons base of acetate and glucosidic protons), 3.67–4.25 (m, 2H, H-10 and remaining sugar protons), 2.48 (m, 2H, H-5 and H-9), 1.48 (s, 3H, Me at C-4). The ms had a molecular ion peak at *m/e* 556 (0.6%). The ^{13}C-nmr ($CDCl_3$) is presented in table 2. Analysis: Calcd for $C_{26}H_{36}O_{13}$: C, 56.11; H, 6.52. Found: C, 56.90, H, 6.70%.

ISOLATION OF STRICTOSIDE (**13**).—The residue from combined fractions 104–155 (1.75 g) from the nonphenolic *n*-butanol solubles chromatographic separation contained a substance that appeared as a brilliant red spot upon tlc development. This residue was passed through Florisil (4 g) with benzene-methanol (3:1) as eluent to collect a single fraction of 120 ml, and its residue (958 mg) was chromatographed on silica gel 60 (100 g) with solvent system-I; 30 ml fractions were collected. The residue from the combined fractions 13–22 (606 mg) was rechromatographed under the same conditions. The residue from fractions 46–50 (242 mg) yielded an homogeneous spot upon tlc analysis.

Strictoside was isolated as an oil with ^{1}H-nmr (D_2O) δ1.38–1.03 (4H, 2H-6 and 2H-7), 1.38 (s, 3H, Me at C-4), 1.95 (m, 1H, H-9), 2.50 (m, 1H, H-5), 3.15–4.02 (protons of sugar and H-8), 5.14 (d, *J* 3.5 Hz, H-1), 5.89 (brs, H-3). The mass spectrum had a molecular ion peak at 332 (0.52%); the ^{13}C-nmr (D_2O) is presented in table 1.

STRICTOSIDE (**13**) PENTAACETATE.—The pentaacetate exhibited the following physical and spectral properties: mp 149–150° (from ethanol); $[\alpha]^{25}D$ −118° (c 3.7, $CHCl_3$); ir ($CHCl_3$) no free hydroxyl bands and νmax 1760–1740 (acetate), 1675, 1605, 1375, 1250, 1050, 995, 910, 900 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 90 MHz) δ1.25–1.84 (4H, 2H-6 and 2H-7), 1.46 (s, 3H, Me at C-4), 2.10, 2.03 (x2), 2.00, 1.97 (5 acetates), 2.38 (m, 1H, H-9), 2.50 (m, 1H, H-5), 4.20–3.70 (two multiplets for protons base of acetates at C-8 and sugar bases), 4.88–5.16 (protons base of acetate plus glucosidic proton), 5.40 (d, *J* 1.9 Hz, H-1), 5.94 (s, 1H, H-3). The mass spectrum had a molecular ion at 542 (0.72%). The ^{13}C-nmr ($CDCl_3$) is presented in table 2. Analysis: Calcd for $C_{25}H_{34}O_{13}$: C, 55.35; H, 6.32. Found: C, 55.84; H, 6.34%.

EMULSIN HYDROLYSIS OF STRICTOSIDE (**13**).—The aglycone exhibited the following physical and chemical properties: tlc Rf 0.59, (solvent system-I); ^{1}H-nmr (Pyr-d_5, 90 MHz) δ6.34 (brs, H-3), 5.50 (d, *J* 5.4 Hz, H-1), 1.55 (brs, 3H, Me at C-4). The ^{13}C-nmr (Pyr-d_5) indicated the presence of nine carbons at δ (ppm) 93.9 (C-1), 136.1 (3), 112.9 (4), 37.8 (5), 29.1 (6), 34.3 (7), 74.9 (8), 50.6 (9), 16.6 (10).

ACETATE OF STRICTOSIDE AGLYCONE.—The diacetate had the following physical and spectral properties: Rf 0.36 (hexane-ethyl acetate 4:1); ^{1}H-nmr ($CDCl_3$) δ6.18 (d, *J* 4.0 Hz, H-1), 6.00 (brs, H-3), 5.00 (m, H-8), 2.60 (m, H-5), 2.35 (m, H-9), 2.03 (Ac), 2.12 (Ac), 1.58 (s, 3H, Me at C-4).

COLUMN CHROMATOGRAPHY OF THE WATER-SOLUBLE FRACTION.—The aqueous fraction (40 g) obtained from the ethanol extract of *M. decapetala* tops was dissolved in 50 ml of water and placed on a charcoal[4] column (250 g) and eluted with increasing amounts of ethanol in water. The effluent was collected in one liter fractions, except the final fraction (fraction 13) which was three liters. Iridoids were found in fractions 7–13.

The iridoid positive fraction (18.5 g) was chromatographed on silica gel #1 (37 g) with chloroform-methanol (9:1) as the eluent. Fractions of 170 ml were collected after an initial 1.7 liter hold-up volume.

ISOLATION OF DECALOSIDE (**2**).—The material from fractions 124–143 (1 g) was chromatographed on silica gel 60 (100 g) and eluted with ethyl acetate-methanol (6:1) with fractions of 14 ml each being collected. Decaloside was isolated from fractions 61–130 as a colorless hygroscopic material having the following properties: mp 190° [lit. 193° (11)]; ^{1}H-nmr (D_2O) δ6.25 (brs, H-3), 5.88 (brs, 2H, H-7 and H-8), 5.13 (d, *J* 7.3 Hz, H-1), 2.69 (m, H-5 and H-9). The ^{13}C-nmr (D_2O) is presented in table 1. The acetate derivative was found to be identical in its physical and spectral data with the reported literature values for decaloside hexacetate (11). The ^{13}C-nmr ($CDCl_3$) for the hexaacetate is presented in table 2.

ISOLATION OF 11-*O*-β-GLUCOSYL DECALOSIDE.—Fractions 158–194 (3 g) of the chromatographic separation of the iridoid-positive fraction yielded a white amorphous precipitate which tended to decompose upon exposure to light. Purification of this fraction through activated charcoal (7 g) with water and methanol as eluents yielded a syrup (2.8 g). A portion of this syrup (2 g) was chromatographed on a Florisil column with chloroform-methanol (3:1) as eluent to obtain 11-*O*-β-glucosyldecaloside as a hygroscopic white powder (210 mg). It exhibited the following spectral properties: ^{1}H-nmr δ6.47 (brs, H-3), 5.91 (brs, 2H, H-7 and H-8), 3.10–4.60 (protons

[4]Norit A, Fischer Sci. Co.

base of hydroxyl functions), 2.77–2.94 (m, 2H, H-5 and H-9); ^{13}C-nmr (D_2O) signals δ98.4 (C-1), 141.2 (3), 113.4 (4), 44.5 (5), 80.8 (6), 135.9 (7), 133.9 (8), 47.5 (9), 69.9 (11), 101.7 (1'), 73.7 (2'), 76.8 (3'), 70.2 (4'), 76.3 (5'), 61.3 (6'), 99.4 (1"), 73.3 (2"), 76.5 (3"), 70.2 (4"), 76.3 (5"), and 61.3 (6").

ACETATE OF 11-*O*-β-GLUCOSYL DECALOSIDE.—The acetate had the following physical and spectral data: mp 153.5°; $[\alpha]^{25}D$ −128° (MeOH) (c 2.8, $CHCl_3$); ir ($CHCl_3$) no free hydroxyl, νmax 1760, 1660, 1380, 1220, 1040 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 90 MHz) δ6.31 (brs, H-3), 6.05 (dd, *J* 6Hz, H-6), 5.89 (dt, *J* 6Hz, H-7), 5.63 (m, H-8), 5.34–4.81 (protons base of acetates and glucosyl), 4.36–3.74 (remaining protons of primary acetates and 2H-11), 3.07–2.79 (two m, H-5 and H-9), 2.08–1.99 (27H, 9Ac); ^{13}C-nmr ($CDCl_3$) δ96.2 (C-1), 140.3 (3), 111.3 (4), 40.2 (5), 81.9 (6), 132.0 (7), 136.1 (8), 47.0 (9), 69.3 (11), 96.4 (1'), 70.8 (2'), 72.8 (3'), 69.3 (4'), 72.2 (5'), 62.0 (6'), 100.1 (1"), 71.5 (2"), 72.0 (3"), 69.3 (4"), 73.1 (5"), 62.0 (6"), plus acetate signals at ~170 and ~20 ppm.

HYDROGENATION OF 11-*O*-β-GLUCOSYL DECALOSIDE.—Rhodium (5%) on charcoal (50 mg) was suspended in 4 ml of ethanol and saturated with hydrogen for six hours. To this, 11-*O*-β-Glucosyl decaloside (200 mg) in 1 ml of water was added; the reaction was maintained under a hydrogen atmosphere at 20° for 3.5 hrs to produce the 3,4,7,8-tetrahydro product. It had the following physical and spectral properties: Rf 0.1 in chloroform-methanol (3:1), ^{1}H-nmr (D_2O) δ5.09 (brs, H-1), 4.47 (H-1'), 4.28–3.16 (protons base of the hydroxyl groups), 1.18–2.07 (H-4, H-6 and 2H-7).

EMULSION HYDROLYSIS PRODUCT OF 3,4,7,8-TETRAHYDRO-11-*O*-β-GLUCOSYL DECALOSIDE.—The aglycone had the following spectral properties: ^{1}H-nmr (Pyr-d_5) δ5.36 (d, *J* Hz, H-1), 4.63 (m, H-6, 4.15–4.41 (m, 2H-11), 4.07 (m, 2H-3), 2.75 and 2.54 (m, H-5 and H-9), 1.70–2.26 (m, H-4, H-8 and H-7); ^{13}C-nmr (Pyr-d_5) δ95.9 (C-1), 63.5 (3), 25.7 (4), 42.0 (5), 75.3 (6), 33.5 (7), 37.3 (8), 46.7 (9), 61.8 (11).

ACETATE OF TETRAHYDROGLUCOSYL DECALOSIDE AGLYCONE.—The triacetate had the following physical and spectral properties: Rf 0.63 in hexane-ethyl acetate (1:1), ^{1}H-nmr ($CDCl_3$) δ6.01 (s, H-1), 5.13 (d, *J* 4.4 Hz, H-6), 4.40–3.40 (m, H-3 and 2H-11), 2.50–2.23 (m, H-5 and H-9), 2.12, 2.06, 2.03 (3 Ac), 1.25–1.90 (2H-7 and 2H-8).

ACETATE OF TETRAHYDRO-1-*O*-β-GLUCOSYL DECALOSIDE.—The acetate had the following spectral data: ^{1}H-nmr ($CDCl_3$) δ5.63 (t, H-6), 5.24–4.75 (m, for protons base of acetates), 4.18–4.14 (m, 2H-11), 2.15–2.02 (9 Ac), 1.87–1.64 (m, H-4, 2H-7 and 2H-8).

ACID METHANOLYSIS OF TETRAHYDROGLUCOSYL DECALOSIDE.—Tetrahydroglucosyl decaloside (95 mg) was dissolved in 1 ml of methanol and stirred for one hour with a cation exchange resin (50 mg, Dowex AG50W-X12, 200–400 mesh, H^+ form). The reaction mixture was then filtered through 50 mg of Amberlite CG-4B (OH^- form). The resin was washed with methanol and the filtrates concentrated *in vacuo*. The residue was chromatographed on silica gel 60 with solvent system-I to give 1-*O*-methyl-tetrahydro-11-glucosyl decaloside with the following physical and spectral data: Rf 0.19, solvent system-I; ^{1}H-nmr (D_2O) δ5.33 (s, H-1), 4.20–3.30 (glycosyl residue), 3.25 (s, OMe), 1.47–1.98 (m, 2H-3, H-6 and 2H-7); ms indicated the presence of M^+-Me at *m/e* 332 (1.6%), M^+-Me-Glu at *m/e* at 171 (14).

ACETATE OF 1-*O*-ME-TETRAHYDRO-GLUCOSYL DECALOSIDE.—The pentaacetate had the following physical and spectral properties: Rf 0.37 in hexane-ethyl acetate (1:1), ^{1}H-nmr ($CDCl_3$) δ5.53 (m, H-1), 5.14–4.81 (complex signal of protons base of acetates), 3.36 (s, Me), 2.16–2.02 (s, 5Ac), 1.99–1.21 (m, H-4, H-6 and 2H-7).

PERMETHYLATION OF TETRAHYDROGLUCOSYL DECALOSIDE.—Tetrahydroglucosyl decaloside (30 ml) was dissolved in 1.2 ml of dimethyl sulfoxide and 0.5 ml of dimethylsulfinyl anion was added. The reaction mixture was stirred at 26° for 1.5 hr. then cooled to 20°, and methyl iodide (1 ml) was added. The reaction mixture was left at 25° for 15 minutes; 20 ml of water was then added, followed by extraction with chloroform. The chloroform-soluble material gave two spots on tlc, Rf 0.40 and 0.38, with benzene—ethanol—water—ammonia hydroxide (200:47:15:1), but no starting material.

The residue (10 mg) was hydrolyzed with sulfuric acid (0.16 ml, 72%) at 0° for one hour, and then 1.44 ml of water added and the temperature maintained at 100° for 4 hr. The reaction mixture was extracted with chloroform and the extract concentrated *in vacuo*. Glc analysis of the residue indicated the presence of 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside as compared with an authentic sample.

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