[Chem. Pharm. Bull. 29(8)2123—2134(1981)]

Lycopodium Triterpenoids. (11).[1] The Structures of Inundoside-A, -B, -C, -D_1, -D_2, -E, -F, and -G, Triterpenoid-glycosides Occurring in *Lycopodium inundatum* L.[2]

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(Received October 21, 1980)

From *Lycopodium inundatum*, Lycopodiaceae, seven new triterpenoid-glycosides (inundoside-A, -B, -D_1, -D_2, -E, -F, and -G) were isolated together with α-onocerin and serratenediol. Their structures were elucidated as serratenediol 3-α-L-arabinopyranoside (A), its 21-acetate (B), its 4′-*O*-*p*-coumaroyl ester (D_1), its 21-*O*-acetyl and 4′-*O*-*p*-coumaroyl ester (D_2), 21-episerratenediol 3-α-L-arabinopyranoside (E), and its 4′-*O*-*p*-coumaroyl ester (F) by chemical and spectroscopic means. The previously reported tohogenol-glycoside (inundoside-C) thus must be tohogenol 3-α-L-arabinopyranoside. The other glycoside, inundoside-G, obtained only as a tetraacetate, is suggested to be serratenediol 3-α-L-arabinopyranoside 2′- or 3′-*O*-*p*-coumaroyl ester on the basis of spectroscopic evidence.

Keywords——Lycopodiaceae; *Lycopodium inundatum*; triterpenoids; serratenediol arabinoside; acylated glycoside; inundosides; modified Smith degradation; ^{13}C-NMR; acylation shift; glycosidation shift

The *Lycopodium* plants characteristically contain triterpenoids of the serratane group,[4] which occur not only as the triterpenoid *per se* and the esters of cinnamic acid derivatives,[5] but also as the glycosides. Only two examples of the glycosides are known to date, which were isolated in 1974 by Tsuda *et al.*[4] from the saponified methanol extract of *Lycopodium inundatum* L. collected at Yanohara, Fukushima prefecture. Those glycosides were characterized as the acetates and identified as a serratenediol-glycoside and a tohogenol–glycoside, respectively.[4] No further structural study has been reported, however.

The present investigation on the same plant, but collected at a different place, Takashima-cho, Shiga prefecture, resulted in the isolation of seven triterpenoid–glycosides with closely related structures, when the methanol extract of the plant was fractionated without saponification. We wish to designate these glycosides as "inundosides." One of these was identical with the previously reported serratenediol–glycoside (inundoside-A)[4] and the others were new compounds. The tohogenol-glycoside (inundoside-C) was not isolated in the present investigation. This paper presents details of the isolation and structure elucidation of these inundosides (A, B, C, D_1, D_2, E, F, and G).

Isolation of Inundosides

The methanol extract of the plant, from which the alkaloid had been removed by washing with 5% AcOH, was fractionated into 5 fractions by Soxhlet extraction with a change of solvent from *n*-hexane to methanol (see "Experimental").

The less polar fraction (Ext. I), on chromatography, gave serratenediol and α-onocerin as reported previously.[4,6] Acetylation of the more polar fractions yielded three glycoside-acetates which were separated by column chromatography. These are the previously reported inundoside-A tetraacetate[4] and two new compounds, inundoside-D tetraacetate and inundoside-G tetraacetate. The latter two possess a *p*-coumaroyl group in addition to acetyl groups as deduced from their nuclear magnetic resonance (NMR) spectra (see below), suggesting that the plant contains acylated glycosides. Therefore, Ext. III—IV were chromatographed

Table I. Characterization of Inundosides

Inundoside	mp. (°C)	IR cm^{-1} (ester CO)	Acyl	Acetate	mp. (°C)
A (**1a**)	>300		——	I-A tetraacetate	>300
B (**2**)	>300	1725	Acetyl	as above	
C (**6a**)	>300		——	I-C tetraacetate	>300
D_1 (**3a**)	286—290	1690	*p*-Coumaroyl	I-D tetraacetate	272—274
D_2 (**4**)	>300	1725, 1703	Acetyl, *p*-coumaroyl	as above	
E (**7a**)	>300		——	I-E tetraacetate	291—293
F (**8a**)	>300	1680	*p*-Coumaroyl	I-F tetraacetate	214—218
G (**5a**)			*p*-Coumaroyl	I-G tetraacetate	>300

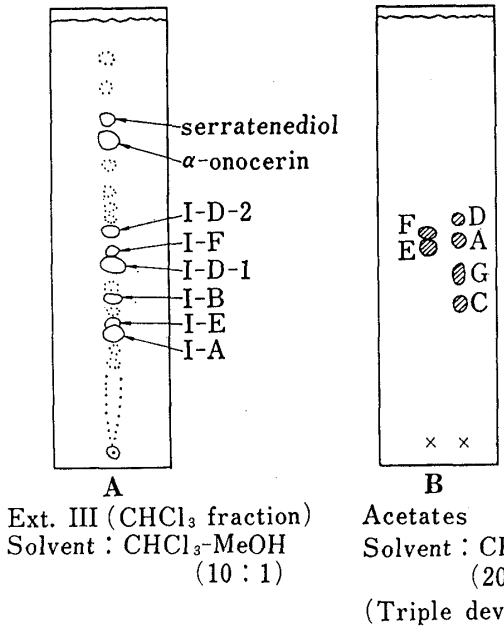


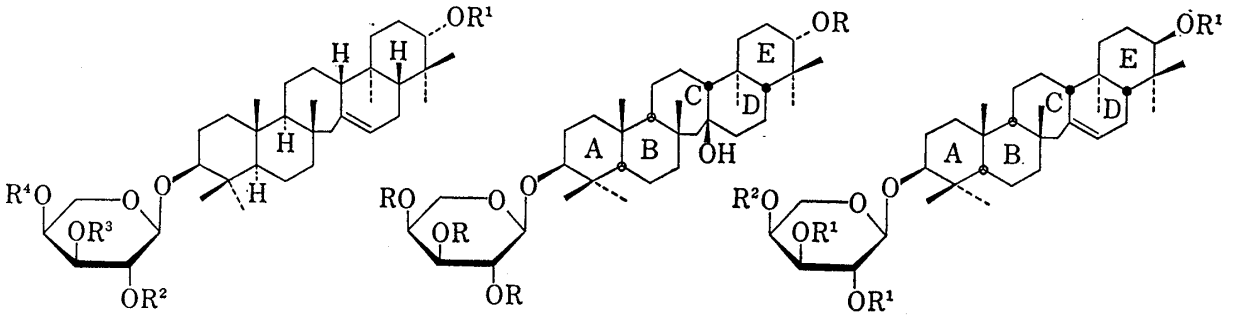
Fig. 1. TLC of Inundosides (A) and Inundoside-acetates (B)

without acetylation to yield inundoside-A, -B, -D_1, -D_2, -E, and -F (details---see "Experimental"). The physical and spectroscopic properties and chromatographic behavior of these glycosides (and also of the acetates) are assembled in Table I and Fig. 1, respectively. It is noteworthy that inundoside-B, -D_1, -D_2, and -F are acylated glycosides: inundoside-D_1 and -F possess a *p*-coumaroyl group, inundoside-B an acetyl group, and inundoside-D_2 has both an acetyl and a *p*-coumaroyl group.

Structures of Inundoside-A, -B, and -C

It is already known[4] that on acid hydrolysis inundoside-A (**1a**) affords isoserratenediol (**9**) and a sugar which reduces Fehling solution. Its formula, $C_{35}H_{58}O_6$, was confirmed by high-resolution EI mass spectroscopy (MS) with a special inlet (IB).[7] Partial deacetylation of inundoside-A tetraacetate (**1b**) with 0.02 N NaOMe in dry MeOH afforded a mono-acetate (**2**) which was identical with inundoside-B (infrared (IR), NMR, and thin layer chromatography (TLC) comparisons). Acid hydrolysis of inundoside-B (**2**) with methanolic hydrochloric acid yielded a mixture of arabinose and methyl arabinoside (a secondary product formed from arabinose) as detected by gas liquid chromatography (GLC) of the trimethylsilyl (TMS) derivatives of the hydrolysate. The aglyconic portion, however, was not obtained in pure form because of acid-catalyzed serratene-isoserratene isomerization.[8]

To obtain clear-cut information on both the aglyconic and the sugar portion, we applied a Smith degradation procedure[9] modified by us (use of lead tetraacetate instead of periodate) to inundoside-B (**2**). The organic solvent-soluble product thus obtained was identified as serratenediol 21-acetate (**11b**).[10] The position of the acetyl group was confirmed by the positive Cotton effect of the derived 3-ketone (**15**).[8,10] GLC of the water-soluble product revealed that the products were ethyleneglycol (**12**) and glycolaldehyde (**13**) (after conversion to the oximes of syn- and anti-form, **14a** and **14b**)[11] (see Fig. 2), both products being derivable from an arabinopyranoside. However, glycerol, which is expected from an arabinofuranoside (*cf.* Chart 3), was not detected, thus indicating that the sugar portion had an arabinopyranoside



1a: $R^1=R^2=R^3=R^4=H$
1b: $R^1=R^2=R^3=R^4=Ac$
2 : $R^1=Ac$, $R^2=R^3=R^4=H$
3a: $R^1=R^2=R^3=H$, $R^4=HO$-C$_6$H$_4$-CH=CHCO-
3b: $R^1=R^2=R^3=Ac$, $R^4=AcO$-C$_6$H$_4$-CH=CHCO-
4 : $R^1=Ac$, $R^2=R^3=H$, $R^4=HO$-C$_6$H$_4$-CH=CHCO-
5a: $R^1=R^4=H$, R^2; $R^3=H$; HO-C$_6$H$_4$-CH=CHCO-
5b: $R^1=R^4=Ac$, R^2; $R^3=Ac$; AcO-C$_6$H$_4$-CH=CHCO-

6a: R=H
6b: R=Ac

7a: $R^1=R^2=H$
7b: $R^1=R^2=Ac$
8a: $R^1=H$, $R^2=HO$-C$_6$H$_4$-CH=CHCO-
8b: $R^1=Ac$, $R^2=AcO$-C$_6$H$_4$-CH=CHCO-

Chart 1

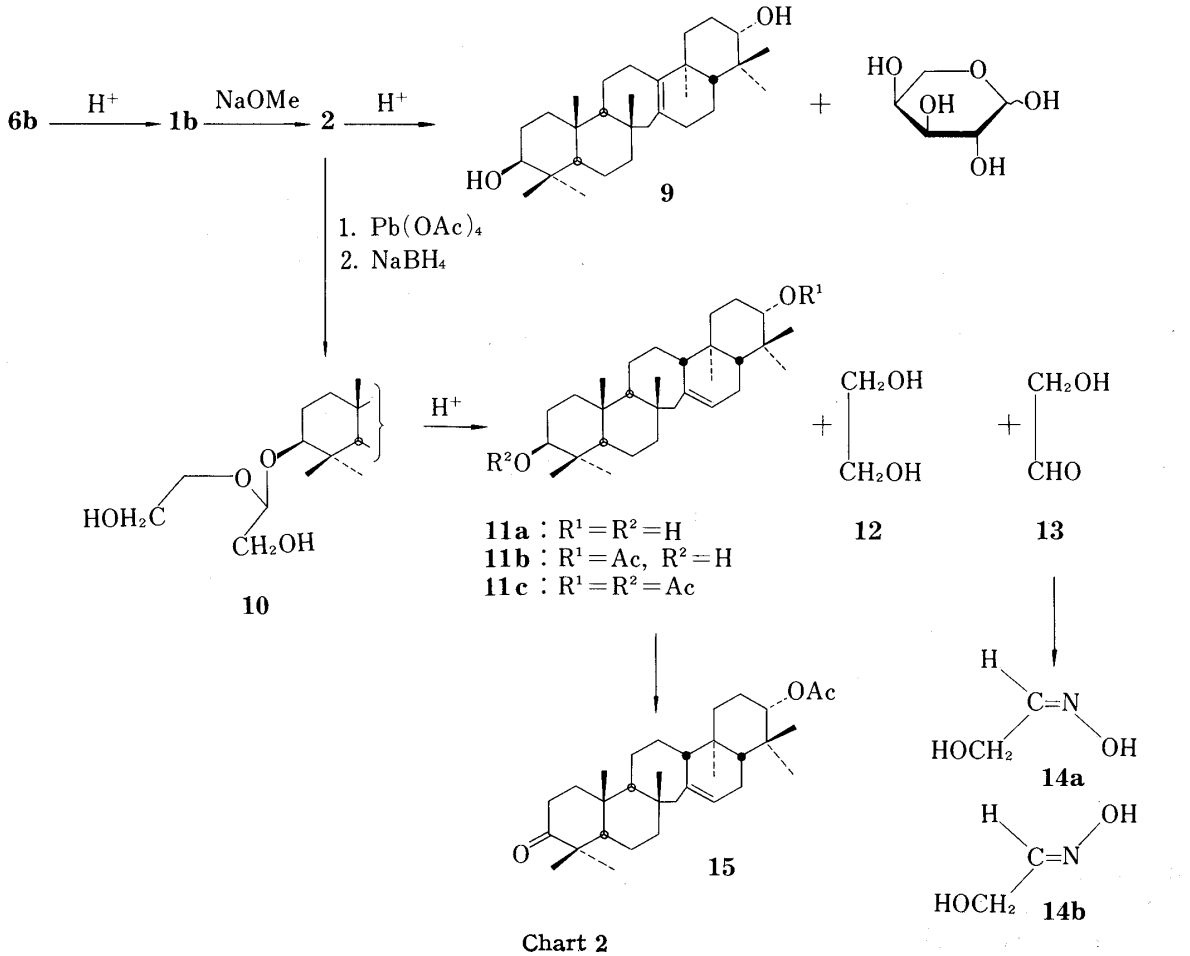


Chart 2

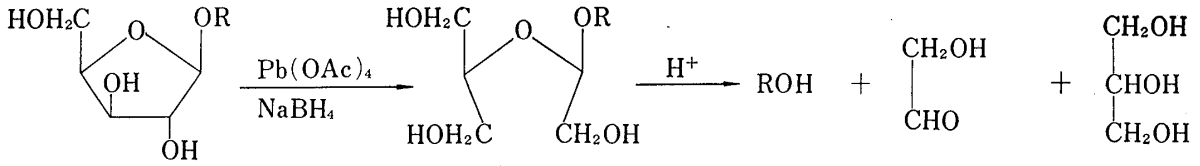


Chart 3. Possible degradation pathway of an arabinofuranoside

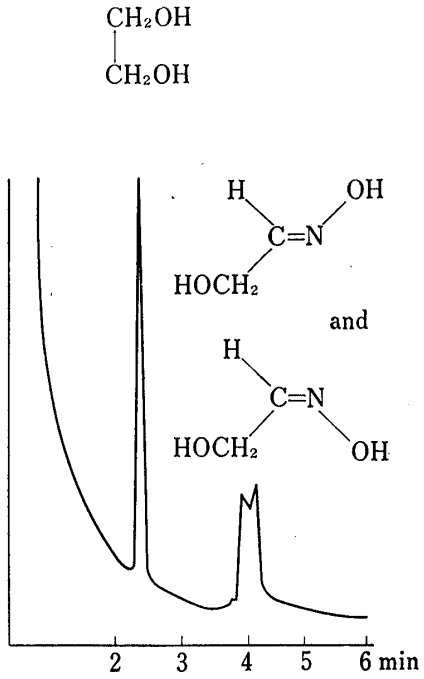


Fig. 2. GLC of the Water-soluble Fraction of the Modified Smith Degradation Product of Inundoside-B

Column temp: 90 °C, N_2: 1.35 kg/cm².

structure. This assignment was supported by the ^{13}C-NMR spectrum of inundoside-A (see below).

The anomeric configuration of the arabinopyranose portion was indicated as α, on the basis of the doublet proton signal of inundoside-A tetraacetate at δ 4.44 with $J=7$ Hz.[12] This assignment was supported by the ^{13}C-NMR spectrum of inundoside-A (**1a**), since the signals of the arabinose moiety were almost identical with those of methyl α-L-arabinopyranoside (**17**)[13] except for those of C-1′, whose slight difference in chemical shift can be attributed to the difference of the aglyconic alcohols[13] (see Table II). The absolute configuration of the arabinose moiety was the remaining problem to be clarified, since arabinose occurs in nature as either the L- or D-form. This was solved as follows.

Tanaka and co-workers[14] and Tori *et al.*[13] reported that, when a chiral secondary alcohol forms a glycopyranoside with a sugar of known absolute configuration, the absolute configuration of the alcohol can be determined from the following ^{13}C-NMR glycosidation shift values: $\Delta\delta_S=\delta$(glycoside)$-\delta$(methyl glycoside), and $\Delta\delta_A$ (at C-α and C-β) $=\delta$(glycoside)$-\delta$(aglycone). The principle of this method is based on the fact that the glycoside which bears substituent(s) on the β carbon anti to the pyranose–ring oxygen (sterically hindered case II) shows markedly different glycosidation shifts from the glycoside which bears substituent (s) on the syn-β carbon (sterically hindered case I) (*cf.* Table IV). It therefore follows that, if the absolute stereochemistry of the aglyconic alcohol and the configuration (α or β) of the glycosidic linkage are known, the absolute configuration of the sugar moiety can immediately be deduced from the values of the glycosidation shifts. The method seems generally applicable not only to hexopyranosides such as glucopyranoside[13,14] and mannopyranoside[14] but also to pentopyranosides such as an arabinopyranoside, although no example of the latter has been reported to date. We therefore prepared methyl oleanolate 3-α-L-arabinopyranoside (**18a**) and the corresponding 3-α-D-arabinopyranoside (**19a**), and examined their glycosidation shifts.

Comparisons of their glycosidation shifts at C-1′, C-3, C-2 ,and C-4 with those of **20** and **21**[14] revealed that the arabinosidation shift values are compatible with the glucosidation shifts, respectively, indicating that the above method is also applicable to arabinopyranosides.

The glycosidation shift values at particular carbons of inundoside-A (and also of the other inundosides···see Table IV) were almost identical with those of methyl oleanolate 3-α-L-arabinopyranoside (**18a**) and distinct from those of methyl oleanolate 3-α-D-arabinopyranoside (**19a**) hence establishing that the arabinopyranoside moiety of inundoside-A has L configuration, since the structure and the absolute configuration of ring A of serratenediol are the same as

those of methyl oleanolate[8] and the glycosidic linkage was proved to be α (see above).

Therefore, inundoside-A is serratenediol 3-α-L-arabinopyranoside (**1a**) and inundoside-B is its 21-monoacetate (**2**). The previously reported inundoside-C should be tohogenol 3-α-L-arabinopyranoside (**6a**), since its tetraacetate (**6b**) was convertible to inundoside-A tetraacetate (**1b**) on treatment with 1% HCl–MeOH.[4]

TABLE II. ^{13}C-NMR Spectral Data for Inundosides and Related Compounds, and the Acylation Shifts (in parentheses)[a]

	1a[b]	3a[c] (3a—1a)	4 (4—1a)	7a	8a (8a—7a)	3b	5b	17[d]	11a[e]	11c	22[e]
Arabinopyranosyl											
1′	106.8	107.3 (+0.5)	107.4 (+0.6)	107.3	107.6 (+0.3)	103.8	103.7	105.9			
2′	72.8	72.7 (−0.1)	72.7 (−0.1)	72.9	72.8 (+0.1)	70.4	70.6	72.2			
3′	74.4	73.2 (−1.2)	73.2 (−1.2)	74.6	73.3 (−1.3)	71.3	71.5	74.4			
4′	69.0	72.1 (+3.1)	72.2 (+3.2)	69.4	72.3 (+2.9)	69.0	69.1	69.1			
5′	66.1	64.2 (−1.9)	64.4 (−1.7)	66.6	64.4 (−2.2)	64.0	63.9	66.6			
Aglycone											
2	26.8	27.0	26.9	26.9	27.1				28.2		28.5
3	88.8	89.1	89.0	88.7	89.1	89.4	89.5		78.2*	80.6*	78.3
4	39.5	39.5	39.7	39.0	39.0				39.5		39.3
14	138.7	138.6	138.6	139.0	139.0	138.6	138.7		138.7	138.6	139.1
15	122.8	122.8	122.4	122.8	122.7	122.8	122.9		122.9	122.8	122.9
21	78.4	78.3	80.8	75.3	75.3	80.8	80.9		78.4*	80.8*	75.5
p-Coumaroyl[f]											
1″		167.3	167.4		167.4	166.2	166.0				
2″		115.5	115.4		115.5	118.2	118.0				
3″		145.2	145.3		145.2	144.8	145.1				
1‴		126.1	125.9		126.0	132.1†	132.2†				
2‴		130.5	130.6		130.6	129.8†	129.9†				
3‴		116.7	116.6		116.7	129.8†	129.9†				
4‴		161.3	161.3		161.3	152.9	153.0				

* These assignments may be reversed in each vertical column.
† These assignments are tentative. For the acylation shifts of phenols, see M. Kobayashi, Y. Terui, K. Tori, and N. Tsuji, *Tetrahedron Lett.*, **1976**, 619.
a) Solvent: pyridine-d_5 at 24 °C.
b) At 60 °C.
c) At 50 °C.
d) S. Seo, Y. Tomita, K. Tori, and Y. Yoshimura, *J. Am. Chem. Soc.*, **100**, 3331 (1978).
e) At 80 °C.
f) For the assignments, *cf.* B. Ternai and K.R. Markham, *Tetrahedron*, **32**, 565 (1976).

Inundoside-D_1 and -D_2

Spectral data for inundoside-D_1 and -D_2 suggested that the former contains a *p*-coumaroyl group and the latter possesses an additional acetyl group (see "Experimental") on the same triterpenoid–glycoside. In fact, both compounds gave the same acetate, inundoside-D tetraacetate (**3b**),[15] on acetylation and the same deacylated glycoside, inundoside-A (**1a**), on saponification. Mild methanolysis of inundoside-D tetraacetate gave methyl *p*-coumarate (**23**) and inundoside-B (**2**), indicating that the *p*-coumaroyl group is linked at the arabinose moiety.

The positions of the acyl groups in inundoside-D_1 and -D_2 were elucidated from the ^{13}C-NMR spectra by comparing the carbon signals of the arabinose moiety with those of inundoside-A (**1a**). The arabinose C-4′ signal of inundoside-D_1 had shifted down-field, and the C-3′ and C-5′ signals had shifted up-field, while the signals of the aglyconic portion of both glycosides

Table III. ^{13}C-NMR Spectral Data for Methyl Oleanolate 3-α-L- and 3-α-D-Arabinopyranosides, **18a** and **19a**, in Pyridine-d_5 (at 24 °C)[a]

Carbon No.	18a	19a	Carbon No.	18a	19a
1	38.7	38.5	19	46.0	46.0
2	26.5	23.7	20	30.7	30.8
3	88.5	84.7	21	33.9	33.9
4	39.4	38.5	22	32.7	32.8
5	55.8	56.1	23	28.1	28.6
6	18.4	18.6	24	16.9	17.1
7	33.1	33.1	25	15.4	15.4
8	39.6	39.6	26	17.1	17.1
9	47.8	47.8	27	26.1	26.1
10	36.9	37.1	28	177.7	177.8
11	23.3	23.4	29	33.1	33.1
12	122.7	122.7	30	23.6	23.7
13	144.0	144.1	OMe	51.5	51.5
14	41.8	41.9	1′	107.2	102.7
15	28.0	28.0	2′	72.7	72.4
16	23.6	23.7	3′	74.4	74.6
17	46.8	46.9	4′	69.2	69.4
18	41.7	41.7	5′	66.5	66.8

a) Signal assignments are based on the results of off-resonance experiments and comparisons with the literature data in $CDCl_3$ (K. Tori, S. Seo, A. Shimaoka, and Y. Tomita, *Tetrahedron Lett.*, **1974**, 4227.)

Table IV. ^{13}C-NMR Arabinosidation Shifts

Glycosides	$\Delta\delta_S$ (C-1′)[a] C-1′	$\Delta\delta_A$ (C-α) C-3	$\Delta\delta_A$ [C-β (*H*)][b] C-2	$\Delta\delta_A$ [C-β (*M*)][b] C-4	Ref.
Hindered Case I					
Dammarenediol-I β-L-Glc (**21**)	−3.2	+6.9	−4.2	−0.8	14)
Me oleanolate α-D-Ara (**19a**)	−3.2	+6.1	−4.5	−0.8	This work
Hindered Case II					
Dammarenediol-I β-D-Glc (**21**)	+1.4	+10.3	−1.2	+0.3	14)
Me oleanolate α-L-Ara (**18a**)	+1.3	+9.9	−1.7	+0.1	This work
Inundoside-A (**1a**)	+0.9	+10.6[c]	−1.4	±0	This work
Inundoside-D_1 (**3a**)	+1.4	+10.9[c]	−1.2	±0	This work
Inundoside-D_2 (**4**)	+1.5	+10.8[c]	−1.3	+0.2	This work
Inundoside-E (**7a**)	+1.4	+10.4[c]	−1.6	−0.3	This work
Inundoside-F (**8a**)	+1.7	+10.8[c]	−1.4	−0.3	This work

a) $\Delta\delta_S = \delta$(glycoside) − δ(Me glycoside)
b) $\Delta\delta_A = \delta$(glycoside) − δ(aglycone), see the text.
c) Calculated by assuming that the C-3 signal of serratenediol is at δ 78.2 ppm. Calculation from the alternative assignment (78.4 ppm) gave values 0.2 ppm less than those in the table.

were almost superimposable. Application of the acylation shift rule[16–18] therefore established that the *p*-coumaroyl group is at C-4′. Comparison of the ^{13}C-NMR spectra of inundoside-D_2 with those of inundoside-D_1 and serratenediol diacetate (**11c**) disclosed that the acetyl group is at C-21 of the aglyconic portion, the signals of sugar portion being superimposable on those of inundoside-D_1 and that of C-21 being identical with that of serratenediol diacetate (**11c**).

Thus, inundoside-D_1 is 4′-*O*-*p*-coumaroyl-serratenediol 3-α-L-arabinopyranoside (**3a**) and inundoside-D_2 is its 21-acetate (**4**).

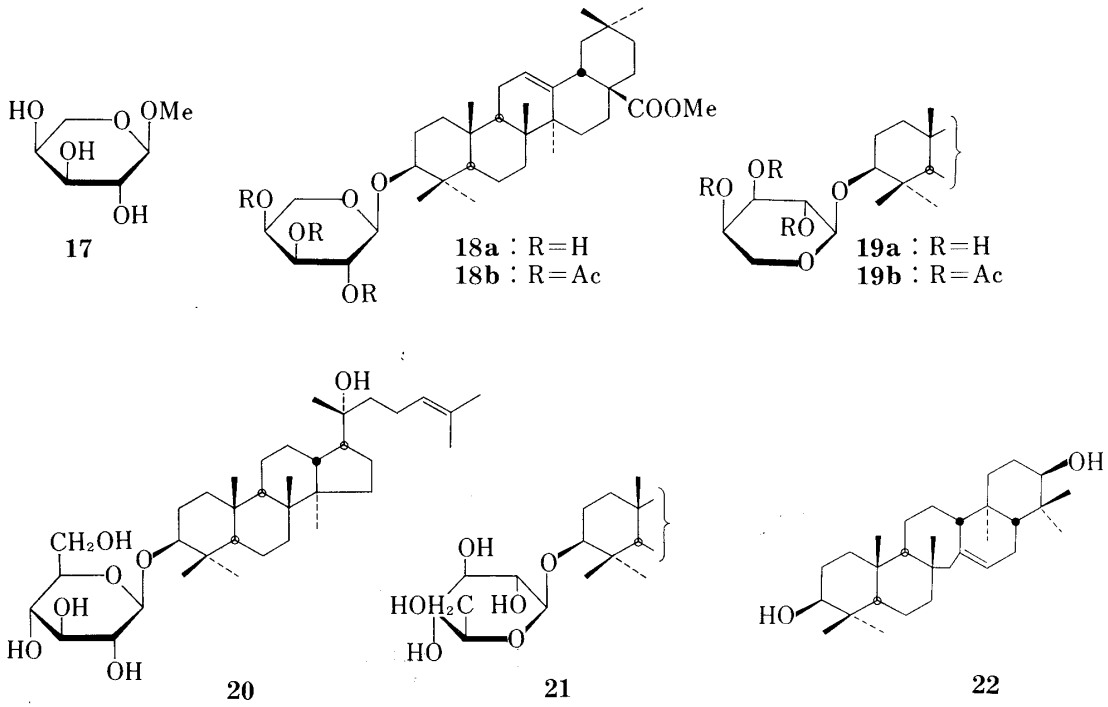


Chart 4

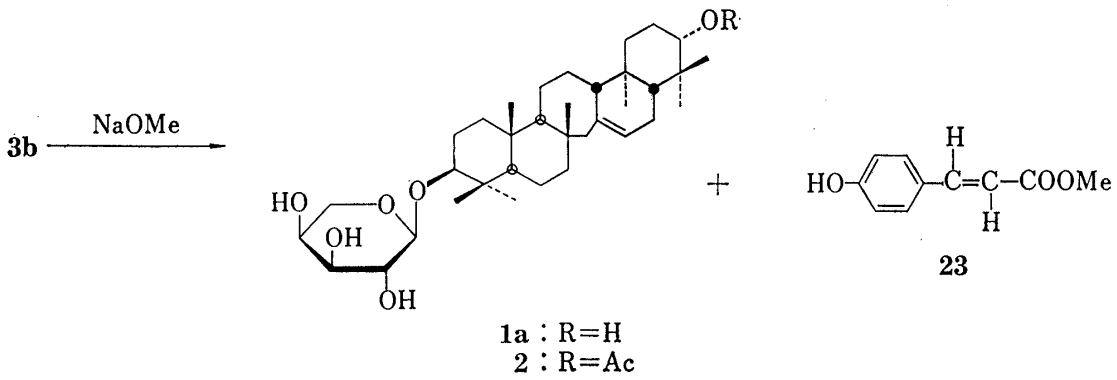


Chart 5

Inundoside-E and -F

Another acylated glycoside, inundoside-F, on methanolysis with NaOMe–MeOH, produced methyl *p*-coumarate and inundoside-E, which was different from inundoside-A (**1a**) and gave the tetraacetate, mp 291—293 °C. The formulae, $C_{35}H_{58}O_6$ for inundoside-E and $C_{44}H_{64}O_8$ for inundoside-F, were suggested from the FD mass spectra.

The ^{13}C-NMR spectra of inundoside-E and -F indicated that they are 21-episerratenediol 3-α-L-arabinopyranoside (**7a**) and its 4′-*O*-*p*-coumaroyl ester (**8a**), respectively. The signals of the sugar moiety of inundoside-E were almost superimposable on those of inundoside-A, but the C-21 signal of its aglycone appeared at a significantly higher field than that of inundoside-A; instead its chemical shift (75.3 ppm) was similar to that of 21-episerratenediol (**22**) (75.5 ppm), in which the 21-OH group has an axial orientation (see Table II). For inundoside-F, the signals of the sugar portion were similar to those of inundoside-D_1, but those of the aglyconic portion were almost identical with those of inundoside-E. The above assignment was supported by the appearance of a broad singlet attributable to H-21 in the ^{1}H-NMR spectra of the acetates (δ 4.68 for **7b** and 4.66 for **8b**).

Inundoside-G

Inundoside-G was isolated in a pure form only as the tetraacetate after acetylation. It was also considered to be a *p*-coumaroyl ester of serratenediol 3-α-L-arabinopyranoside for the following reasons. Its ^{13}C-NMR spectrum was almost identical with that of inundoside-D tetraacetate (**3b**) throughout the whole region (*cf.* Table II). The ^{1}H-NMR spectrum was also quite similar to that of **3b**. However, clear differences were seen in the signals of the acetyl methyls and in the shape of the anomeric proton signal.

Among the four acetyl methyls of inundoside-G tetraacetate (δ 2.03, 2.04, 2.11, 2.31), the peak at δ 2.31 must be due to the acetyl group on *p*-coumarate, since inundoside-D tetraacetate (**3b**) and inundoside-F tetraacetate (**8b**) exhibited similar peaks at δ 2.33 and 2.32, while inundoside-A tetraacetate (**1b**) and inundoside-E tetraacetate (**7b**) lacked the corresponding signal. The peak at δ 2.11 is attributable to the acetyl group at position 4′ of the arabinose moiety, since **1b** and **7b** showed the peak at δ 2.13 and 2.13, while **3b** and **8b**, in which 4′-*O* is occupied by a different acyl group, lacked a peak at this position.

The above evidence led to the suggestion that inundoside-G is the 2′-or 3′-*O*-*p*-coumaroyl ester of **1a** (**5a**).[19]

Isolation of inundoside-G tetraacetate (**5b**) indicates that the plant contains a compound carrying a *p*-coumaroyl group at the 2′ or 3′ position of inundoside-A. These acyl groups might migrate to 4′ during chromatographic separation, since it was indicated that acyl migration, including *trans* 2⇌3 migration, occurs easily in acyl β-glucosides.[20] This must also be true in acyl-arabinosides. We therefore consider that at least a portion of inundoside carrying the acyl group at position 4′ may be products of such an acyl migration. Details of this problem will be reported in a future communication.

Experimental

Mp's were taken on a Yanagimoto micro hot-stage mp apparatus. IR spectra were taken as KBr discs using a Jasco IR-G spectrometer and are given in cm^{-1}. ^{1}H-NMR (at 100 MHz) and ^{13}C-NMR (at 25.0 MHz) spectra were recorded on a JEOL PS-100 CW type or on a JEOL FX-100 FT NMR spectrometer. All compounds listed in Table II gave ^{13}C-NMR signals in agreement with the molecular formulae shown in the text. 60 MHz ^{1}H-NMR were taken on a JMN PMX-60 spectrometer. FD mass spectra were taken with a Hitachi M-80 or a JEOL D-300 machine and EI-IB mass spectra[7] were recorded on a Hitachi M-80 machine. GLC analyses were carried out with a Shimadzu GC4CM-PF gas chromatograph coupled to an FID detector, using a glass column (2 m × 3 mm, I.D.) packed with 1.5% OV-1 on Shimalite W, with N_2 as a carrier gas. TMS derivatives were prepared according to Sweeley *et al.*[21]

Wakogel C-200 (silica gel) was used for column chromatography. For TLC, Kieselgel 60F_{254} precoated plates were used and spots were developed by spraying 1% $Ce(SO_4)_2$ in 10% H_2SO_4 and heating at 100°C until coloration took place. Preparative TLC (PTLC) was carried out on GF_{254} plates (20 × 20 cm) of 0.5 mm thickness and the zone containing *p*-coumaroyl derivatives was monitored by ultraviolet (UV) (254 nm) absorption measurement.

Acetylation was done by heating a compound with a large excess of pyridine–Ac_2O (2: 1) mixture for 30 min at 80°C and keeping it overnight at room temp. For saponification, 5% KOH–MeOH was used.

Extraction of Lycopodium Inundatum——*L. inundatum* (170 g) collected at Takashima-cho, Shiga Pref., in Oct. 1975, was cut and extracted with hot MeOH (2 L × 5, each 8 h). The combined extract was concentrated *in vacuo* to yield a syrup (*ca.* 200 ml) which was stirred with 5% AcOH (500 ml) and allowed to stand overnight. The ppt was collected by filtration, washed with water, and dried to yield a neutral–acidic fraction (28 g). This was extracted successively in a Soxhlet apparatus with *n*-hexane, ether, $CHCl_3$, $CHCl_3$–MeOH, and MeOH, each for 18 h, yielding the following extracts.

Ext. I,	*n*-hexane	9.0 g
Ext. II,	ether	3.9 g
Ext. III,	$CHCl_3$	9.9 g
Ext. IV,	$CHCl_3$–MeOH	4.0 g
Ext. V,	MeOH	1.0 g

Each extract (except Ext. V) left a ppt which was collected by filtration.

A portion (2.4 g) of the filtrate from Ext. I, on chromatography, gave α-onocerin (13 mg), mp 223—225°C, together with a waxy substance, mp 79—80°C, IR: 1735, and mp 83—83.5°C, IR: no CO absorption.

A portion (0.5 g) of the ppt from Ext. I was divided into a benzene-soluble part and a benzene–insoluble part. The benzene–insoluble part (0.14 g), on acetylation, gave α-onocerin diacetate (90 mg), mp 220—222°C. Chromatography of the benzene–soluble part in $CHCl_3$ gave serratenediol **11a** (15 mg), mp 297—300°C.

A portion (1 g) of the ppt from Ext. II was acetylated. Chromatography of the resulting acetate in $CHCl_3$ gave inundoside-D tetraacetate **3b**[15] (91 mg), mp 270—272°C, colorless needles from *n*-hexane–benzene, and inundoside-A tetraacetate **1b** (5 mg), mp>300°C, colorless needles from $CHCl_3$–MeOH. These products were identical (IR, proton magnetic resonance (PMR), and TLC comparisons) with the corresponding compounds described below. Further elutions with the same solvent and purification of the eluates by PTLC gave inundoside-G tetraacetate **5b** (15 mg), mp>300°C, colorless needles from $CHCl_3$–MeOH. IR: 1700, 1240 (ester), 1600, 1500 (aromatic). ^{1}H-NMR (100 MHz, $CDCl_3$): –Ç–CH_3 0.70, 0.76, 0.83(2), 0.86, 0.91(2); OAc 2.03, 2.04, 2.11, 2.31; H-3 2.9—3.2 (1H); H_2-5′ 3.5—4.2 (2H); H-21 4.35—4.65 (1H); H-1′ 4.50 (1H, d, J=5.6 Hz); H-2′, H-3′, H-4′, =CH– 4.5—5.4 (4H); ArCH–CHCOO 6.32, 7.64 (each 1H, d, J=16 Hz); Ar–H 7.10, 7.52 (each 2H, d, J=8 Hz). ^{1}H-NMR (100 MHz, Py-d_5): –Ç–CH_3 0.73, 0.82, 0.89, 0.93, 0.96(2), 1.12; OAc 2.01, 2.08, 2.18, 2.22. MS (FD) ($C_{54}H_{74}O_{13}$=888): 911 $(M+Na)^+$, 888 (M^+).

Ext. III (9.9 g) was dissolved in $CHCl_3$–MeOH (1: 1) and adsorbed on SiO_2, which was dried and placed (6 cm layer) on the top of an SiO_2 column (4.5×29 cm, slurried with $CHCl_3$). The column was eluted with $CHCl_3$–MeOH (25: 1) to yield 40 fractions of 100 ml each (recovery, 4.2 g), from which inundosides were isolated as follows.

Isolation of Inundoside-D$_2$ (4)——Frs. 2—4, on standing in $CHCl_3$–MeOH, deposited α-onocerin (30 mg). The mother liquor (710 mg) after removal of α-onocerin was rechromatographed in a manner similar to that described above. Elution with $CHCl_3$–MeOH (55: 1) gave inundoside-D_2 **4** (58 mg), mp>300°C, colorless needles from $CHCl_3$–MeOH. IR: 3400 (br), 1728, 1703, 1629, 1603, 1585, 1512, 1250. ^{1}H-NMR (100 MHz, Py-d_5): –Ç–CH_3 0.73, 0.87(2), 0.94, 0.96, 1.04, 1.35; OAc 2.08; H-1′ 4.86 (1H, d, J=7.0 Hz); ArCH=CHCOO 6.52, 7.91 (each 1H, d, J=16 Hz); Ar–H 7.15, 7.43 (each 2H, d, J=8.5 Hz). MS (FD) ($C_{46}H_{66}O_9$=762): m/z 785 $(M+Na)^+$, 762 (M^+), 639, 598, 484.

On acetylation it gave the acetate, mp 268—270°C, colorless needles from *n*-hexane–benzene; this product was identical (TLC, IR, and mixed mp comparisons) with inundoside-D tetraacetate **3b** (see below).

Isolation of Inundoside-F (8a)——Frs. 5—7, on standing in MeOH, deposited a pale yellow powder. Several crystallizations of this from $CHCl_3$ yielded α-onocerin (45 mg). The mother liquor (410 mg) after removal of α-onocerin was rechromatographed to yield, from the $CHCl_3$–MeOH (50: 1) eluate, further crops of α-onocerin (63 mg) and inundoside-D_2 (40 mg). Subsequent elutions with the same solvent gave inundoside-F **8a** (15 mg), mp>300°C, colorless needles from $CHCl_3$–MeOH. IR: 3300 (br), 1678, 1629, 1603, 1585, 1512, 1255. ^{1}H-NMR (100 MHz, Py-d_5): –Ç–CH_3 0.79, 0.83(2), 0.96, 1.04, 1.17, 1.35; H-1′ 4.83 (1H, d, J=7 Hz); ArCH=CHCOO 6.54, 7.93 (each 1H, d, J=16 Hz); Ar–H 7.16, 7.44 (each 2H, d, J=8.5 Hz). MS (FD) ($C_{44}H_{64}O_8$=720): m/z 743 $(M+Na)^+$, 720 (M^+).

On acetylation it gave the tetraacetate **8b**, mp 214—218°C, colorless prisms from *n*-hexane–ether. ^{1}H-NMR (100 MHz, $CDCl_3$): –Ç–CH_3 0.70, 0.77, 0.83(2), 0.86, 0.94(2); OAc 2.01, 2.06, 2.08, 2.32; H-3 2.9—3.2 (1H, m), H_2-5′ 3.4—4.2 (2H); H-1′ 4.48 (1H, d, J=7 Hz); H-21 4.66 (1H, bs); H-2′, H-3′, H-4′, –CH= 5.0—5.4 (4H); Ar–H 7.12, 7.56 (each 2H, d, J=8 Hz).

Inundoside-F (36 mg) was also obtained from Ext. IV by chromatography and PTLC.

Isolation of Inundoside-B (2) and Inundoside-D$_1$ (3a)——Frs. 8—10 (540 mg) were pooled and rechromatographed. The first several fractions eluted with $CHCl_3$–MeOH (25: 1), when kept in $CHCl_3$–MeOH, gave inundoside-B **2** (20 mg) as a white powder. It formed colorless needles after several crystallizations from MeOH, mp>300°C. IR: 3400 (br), 1725, 1250. ^{1}H-NMR (100 MHz, Py-d_5): –Ç–CH_3 0.72, 0.86(2), 0.92, 0.95, 0.99, 1.28; OAc 2.07; H-1′ 4.80 (1H, d, J=7 Hz). MS (FD) ($C_{37}H_{60}O_7$=616): m/z 655 $(M+K)^+$, 639 $(M+Na)^+$, 616 (M^+), 484.

On acetylation it gave the acetate, mp>300°C, which was identical (IR and TLC comparisons) with inundoside-A tetraacetate **1b** (see below).

The mother liquor after removal of inundoside-B, on standing in $CHCl_3$–MeOH (1: 1), deposited a pale yellow powder which was washed with MeOH and crystallized from $CHCl_3$–MeOH (40: 3) to give inundoside-D_1 **3a** (130 mg). Further purification of this product by chromatography with $CHCl_3$–MeOH (44: 1) gave a pure specimen (90 mg), mp 286—290°C, colorless needles from $CHCl_3$–MeOH. IR: 3400 (br), 1684, 1630, 1605, 1584, 1514, 1200. ^{1}H-NMR (60 MHz, Py-d_5): –Ç–CH_3 0.75, 0.80, 0.88, 0.98, 1.05, 1.13, 1.30; H-1′ 4.75 (1H, d, J=6.5 Hz); ArCH=CHCOO 6.40, 7.75 (each 1H, d, J=16 Hz); Ar–H 7.01, 7.32 (each 2H, d, J=8.5 Hz). MS (FD) ($C_{44}H_{64}O_8$=720): m/z 743 $(M+Na)^+$, 720 (M^+).

On acetylation it gave inundoside-D tetraacetate **3b**,[15] mp 272—274°C, colorless needles from *n*-hexane–benzene. IR: 1750, 1730, 1235 (ester), 1635, 1600, 1500 (aromatic). ^{1}H-NMR (100 MHz, $CDCl_3$): –Ç–CH_3 0.70, 0.78, 0.84(2), 0.86, 0.92, 0.94; OAc 2.03, 2.08(2), 2.33; H-3 2.9—3.2 (1H, m); H_2-5′ 3.68, 4.12 (each 1H, AB of ABX pattern, J_{AB}=13 J_{AX}<1, J_{BX}=3 Hz); H-1′ 4.50 (1H, d, J=7 Hz); H-21 4.55 (1H, m); H-2′, H-3′, H-4′, –CH= 5.00—5.42 (4H); ArCH=CHCOO 6.52, 7.73 (each 1H, d, J=16 Hz); Ar–H 7.16, 7.61 (each 2H, d, J=8 Hz). MS (FD) ($C_{54}H_{74}O_{13}$=888): m/z 911 $(M+Na)^+$, 888 (M^+), 346 $(M-C_2H_2O)^+$.

Inundoside-D_1 was also obtained from Ext. IV (15 mg) and from the ppt of Ext. II (15 mg) by chromatography and PTLC.

Isolation of Inundoside-E (7a)——Frs. 14—16 were subjected to PTLC (solvent: $CHCl_3$–MeOH=10: 1) to obtain more mobile and less mobile fractions. The former fraction (150 mg) was a mixture of at least three compounds. The latter fraction, after several crystallizations from $CHCl_3$–MeOH, gave inundoside-E **7a** (31 mg) as colorless needles, mp>300°C. IR: 3400 (br). ^{1}H-NMR (100 MHz, Py-d_5): $-\overset{|}{\underset{|}{C}}-CH_3$ 0.82(3), 0.96, 0.99, 1.17, 1.29; H-1′ 4.78 (1H, d, J=6.4 Hz). MS (FD) ($C_{35}H_{58}O_6$=574): m/z 597 $(M+Na)^+$, 574 (M^+), 442.

On acetylation it gave the tetraacetate **7b**, mp 291—293°C, colorless prisms from $CHCl_3$–MeOH. ^{1}H-NMR (100 MHz, $CDCl_3$): $-\overset{|}{\underset{|}{C}}-CH_3$ 0.70, 0.76, 0.82, 0.84, 0.86, 0.92, 0.94; OAc 2.02, 2.05, 2.08, 2.13; H-3 2.95—3.2 (1H); H_2-5′ 3.61, 4.03 (each 1H, AB of ABX pattern, J_{AB}=13, J_{AX}<1, J_{BX}=3 Hz); H-1′ 4.45 (1H, d, J=7 Hz); H-21 4.68 (1H, bs); H-2′, H-3′, H-4′, =CH– 4.9—5.4 (4H). *Anal.* Calcd for $C_{43}H_{66}O_{10}$: C, 69.51; H, 8.95. Found: C, 69.29; H, 8.62.

Inundoside-E (20 mg) was also obtained from Ext. IV by chromatography and PTLC.

Isolation of Inundoside-A (1a)——Frs. 19—21, after several crystallizations from $CHCl_3$–MeOH, gave inundoside-A **1a** (75 mg), mp>300°C, colorless needles from $CHCl_3$–MeOH. IR: 3400 (OH). ^{1}H-NMR (60 MHz, Py-d_5): $-\overset{|}{\underset{|}{C}}-CH_3$ 0.78, 0.83, 0.92, 0.97, 1.08, 1.17, 1.23; H-1′ 4.71 (1H, d, J=6 Hz). MS (FD): m/z 597 $(M+Na)^+$, 574 (M^+). MS (EI-IB at 20 eV): m/z Found, 574.4247 (Calcd $C_{35}H_{58}O_6$ 574.4230), 425.3789 (Calcd $M^+-C_5H_9O_5$ 425.3781).

On acetylation it gave inundoside-A tetraacetate **1b**, mp>300°C, colorless needles from $CHCl_3$–MeOH. $[\alpha]_D^{17}$=+15° (c=0.85 in $CHCl_3$). IR: 1740, 1225. ^{1}H-NMR (100 MHz, $CDCl_3$): $-\overset{|}{\underset{|}{C}}-CH_3$ 0.68, 0.75, 0.79, 0.81, 0.83, 0.90(2); OAc 2.01, 2.05(2), 2.13; H-3 2.9—3.2 (1H, m); H_2-5′ 3.61, 4.01 (each 1H, AB of ABX pattern, J_{AB}=13, J_{AX}<1, J_{BX}=3 Hz); H-1′ 4.44 (1H, d, J=7 Hz); H-21 4.50 (1H, m); H-2′, H-3′, H-4′, =CH– 4.95—5.40 (4H). MS (FD) ($C_{43}H_{66}O_{10}$=742): m/z 765 $(M+Na)^+$, 742 (M^+).

This product was identical with previously reported serratenediol-glycoside tetraacetate.[4] Saponification of this compound regenerated inundoside-A **1a**, mp>300°C, colorless needles from $CHCl_3$–MeOH.

Partial Deacetylation of Inundoside-A Tetraacetate (1b)——A mixture of inundoside-A tetraacetate **1b** (48 mg) and 0.2 N NaOMe (1 ml) in dry MeOH (10 ml) was stirred at room temp. for 4.5 h and heated under reflux for 1.5 h. The mixture was neutralized with Dowex-50(H^+) (*ca.* 100 mg) and the crystals which separated were collected mechanically and recrystallized from MeOH to give inundoside-A monoacetate **2** (35 mg), mp>300°C, as colorless needles. This product was identical with inundoside-B as judged by comparison of their IR and NMR spectra, and TLC behavior.

Acid Hydrolysis of Inundoside-B (2)——Inundoside-B **2** (15 mg) in 2.8 N methanolic HCl (2.5 ml) was heated under reflux for 4 h, then the mixture was cooled and filtered. The ppt showed two spots on TLC corresponding to (iso-)serratenediol and (iso-)serratenediol 21-acetate. The filtrate was concentrated and shaken with $CHCl_3$ and water. The water layer was neutralized with Dowex 1×8 (HCO_3^-) and concentrated to dryness. The residue was converted to a TMS derivative and analyzed by GLC. The peaks corresponding to arabinose and methyl arabinoside were detected between 6 and 12 min. Column temp.: 150°C, N_2: 1.2 kg/cm^2. The peaks were identical with those of authentic samples of arabinose and methyl arabinoside prepared by methylation of arabinose with MeOH and Dowex-50(H^+).

Modified Smith Degradation of Inundoside-B (2)——A mixture of inundoside-B **2** (8 mg) and $Pb(OAc)_4$ (25 mg) in pyridine (4 ml) was stirred for 3 h at room temp. then, after addition of further reagent (20 mg), was kept overnight at room temp. The excess reagent was decomposed by addition of oxalic acid until the mixture was negative to the iodine–starch test. After dilution with water, the mixture was extracted with $CHCl_3$ and the organic layer was washed with water, dried over Na_2SO_4, and concentrated to dryness to yield a white solid. This was dissolved in $CHCl_3$–EtOH (1: 1) (10 ml) and reduced with $NaBH_4$ (35 mg) overnight at room temp. After decomposition of excess $NaBH_4$ with AcOH, water was added, and the mixture was extracted repeatedly with $CHCl_3$. The combined extract was washed with water, dried, and concentrated to give a residue **10** (5.5 mg), which crystallized in fine needles from methanol and had mp 278°C. These crystals **10** (5.1 mg) in $CHCl_3$ (1 ml) and MeOH (1 ml) were hydrolyzed with 5% HCl (3 drops) overnight at room temp. The product was taken up in $CHCl_3$ and the solution was washed with water, dried, and concentrated to give a white solid. Crystallization of this from methanol afforded fine needles (3.4 mg), mp 279—280°C; this product was identified as serratenediol 21-monoacetate **11b**,[10] by mixed mp, and IR and TLC comparisons with an authentic sample.

The aqueous layer was adjusted to pH 4 by addition of NaOAc, and warmed with $NH_2OH\cdot HCl$ (36 mg) at 80 °C for 1 h, then concentrated to dryness. The residue was dried overnight in a P_2O_5 desiccator, converted to the TMS derivative, and analyzed by GLC. The following peaks were observed: ethyleneglycol **12** (t_R 2.4 min) and glycolaldehyde oximes, **14a** and **14b** (t_R 3.9 and 4.1 min). Column temp., 90°C, N_2: 1.35 kg/cm^2.[11] The peaks were identified by co-GLC with authentic specimens.

Methyl Oleanolate 3-α-D-Arabinopyranoside (19a)——A solution of methyl oleanolate (1 g) in dry benzene (40 ml) and nitromethane (40 ml) was heated on an oil-bath, then a half of the solvent was distilled off to remove moisture as an azeotropic mixture. $Hg(CN)_2$ (0.54 g) and 2,3,4-tri-O-acetyl-β-D-arabinopyranosyl

bromide (0.73 g) were added to the cooled mixture and the whole was stirred at 60 °C with occasional monitoring of the reaction by TLC. After 8 h, additional $Hg(CN)_2$ (0.57 g) and the bromide (0.77 g) were added, and stirring was continued for a further 7 h. The precipitated white solid was removed by filtration and the filtrate was shaken with $CHCl_3$ and sat. $NaHCO_3$ solution. The $CHCl_3$ layer was washed with water, dried, and concentrated to dryness to leave a gum, which was purified by chromatography. Elution of the column with benzene–acetone (50: 1) gave the α-D-arabinopyranoside triacetate **19b** (1.07 g), mp 148—151°C, as colorless needles from MeOH. ^{1}H-NMR (60 MHz, $CDCl_3$): –C(CH$_3$)–CH$_3$ 0.74, 0.77, 0.93(3), 1.03, 1.13; OAc 2.03, 2.05, 2.12; COOMe 3.60; H-1′ 4.48 (1H, d, J=7 Hz). *Anal.* Calcd for $C_{42}H_{64}O_{10}$: C, 69.20; H, 8.85. Found: C, 69.47; H, 8.82.

The triacetate **19b** (0.43 g) in dry MeOH (20 ml) was treated with 0.02 N NaOMe (3 ml) for 1 h at room temp. The mixture was neutralized with Dowex-50(H^+) (1 h stirring), filtered, and the resin was washed with methanol. The combined filtrate and washing was concentrated to leave a solid which, on crystallization from MeOH, gave methyl oleanolate 3-α-D-arabinopyranoside **19a**, mp 306—307°C, as colorless needles (195 mg). ^{1}H-NMR (100 MHz, Py-d_5): –C(CH$_3$)–CH$_3$ 0.83, 0.96(2), 0.94(2), 1.23(2); COOMe 3.70; H-1′ 4.69 (1H, d, J=7 Hz). $[\alpha]_D^{16}$=+57.1° (c=1.0 in C_5H_5N). *Anal.* Calcd for $C_{36}H_{58}O_7$: C, 71.72; H, 9.70. Found: C, 71.50; H, 9.76.

Methyl Oleanolate 3-α-L-Arabinopyranoside (18a)——The triacetate **18b** of the L-isomer was prepared similarly from methyl oleanolate and 2,3,4-tri-O-acetyl-β-L-arabinopyranosyl bromide, as an amorphous powder from MeOH. ^{1}H-NMR (60 MHz, $CDCl_3$): –C(CH$_3$)–CH$_3$ 0.74, 0.77, 0.93(4), 1.13; OAc 2.00, 2.03, 2.11; COOMe 3.61; H-1′ 4.44 (1H, d, J=7 Hz). These data coincide with those given in the literature.[22]

Deacetylation of the triacetate as described for the D-isomer gave methyl oleanolate 3-α-L-arabinopyranoside **18a**, mp 222—224.5°C, (lit.[18] mp 222.5—224.5°C), as colorless needles from MeOH. ^{1}H-NMR (100 MHz, Py-d_5): –C(CH$_3$)–CH$_3$ 0.82, 0.89, 0.94(3), 1.24(2); COOMe 3.69; H-1′ 4.71 (1H, d, J=7 Hz). The data coincide with those given in the literature.[22]

Methanolysis of Inundoside-D Tetraacetate (3b)——A solution of inundoside-D tetraacetate **3b** (15 mg) in 0.056 N NaOMe–dry MeOH (3.6 ml) was heated under reflux for 3.5 h with stirring. The white precipitate was collected by filtration and separated into two compounds by PTLC. The more mobile compound (2.2 mg), mp>300°C, colorless needles from $CHCl_3$–MeOH, was identified as inundoside-B **2** by TLC and IR comparisons with an authentic sample. The less mobile compound was considered to be inundoside-A on the basis of TLC.

The filtrate obtained above was neutralized with Amberite IR-120(H^+), and concentrated to dryness. The residue, on standing in $CHCl_3$–MeOH, precipitated fine needles (0.9 mg), mp>300°C; this product was identical with inundoside-A **1a** on the basis of TLC and IR comparisons. The mother liquor after removal of inundoside-A was purified by PTLC to yield pale yellow plates (1.1 mg) (from aq. EtOH), mp 135—138°C; this product was identical with methyl *p*-coumarate **23** as judged by mixed mp, and TLC and IR comparisons with an authentic specimen (lit. mp 137°C).[23]

Methanolysis of Inundoside-F (8a)——Inundoside-F **8a** (15 mg) and 0.2 N NaOMe (3 ml) in MeOH (12 ml) were heated under reflux for 3 h. The mixture was neutralized with Dowex-50(H^+) and filtered. The filtrate was concentrated to dryness, leaving a white solid which showed two spots on TLC corresponding to methyl *p*-coumarate **23** and inundoside-E **7a**. Acetylation of this mixture and purification of the product by column chromatography gave prisms, mp 290—293°C (from $CHCl_3$–MeOH), which were identical (mp, TLC, and NMR) with inundoside-E tetraacetate **7b**.

Acknowledgement The authors thank Mr. Y. Itatani of this Faculty for NMR measurements. One of the authors (M. K.) also thanks Profs. O. Tanaka and K. Yamasaki, and Dr. R. Kasai, Hiroshima University, for advice on the ^{13}C-NMR assignment. A part of this work was supported by a Naito Research Grant (1978), for which we are grateful.

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