Plant Constituents Biologically Active to Insects. VI.[1] Antifeedants for Larvae of the Yellow Butterfly, *Eurema hecabe mandarina*, in *Osmunda japonica*. (2)

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Three antifeedants for larvae of the yellow butterfly, *Eurema hecabe mandarina* DE L'ORZA, were isolated from *Osmunda japonica* THUNB. and identified as osmundalin, parasorboside and methyl (3*S*,5*S*)-5-hydroxy-3-(β-D-glucopyranosyloxy)hexanoate. In the course of isolation of the antifeedants, a new glycoside, dihydroisoosmudalin (9), was isolated together with maltol β-D-glucopyranoside, 2-deoxy-L-ribopyranolactone, 5-hydroxymethyl-2-furfural and glycerin. The structure of 9 was elucidated as (4*R*,5*S*)-5-(β-D-glucopyranosyloxy)hexan-4-olide on the basis of chemical and spectroscopic evidence.

Keywords antifeedant; *Eurema hecabe mandarina*; *Osmunda japonica*; osmundalin; parasorboside; dihydroisoosmundalin; glucoside

Previously we isolated three antifeedants (**1**, **2** and succinic acid) for larvae of the yellow butterfly, *Eurema hecabe mandarina* DE L'ORZA, as well as **3** and **4** (exhibiting insignificant antifeeding activity), from *Osmunda japonica* THUNB. (Japanese name, zenmai)[1] (Chart 1). Further investigation of this plant led to the isolation of three additional antifeedants (**5**, **6** and **7**) together with five other compounds, including a new glycoside. This paper describes the identification and the feeding-inhibitory activities of these compounds.

The dried whole plants of *O. japonica* were successively extracted with hexane, ether and MeOH. Since three antifeedants had previously been isolated from the ether extract,[1] this time the MeOH extract was investigated. The extract was partitioned between chloroform and water, and the water-soluble fraction was subjected to droplet countercurrent chromatography (DCC). The antifeeding-active fraction was chromatographed on a silica gel column. One of the resulting fractions, exhibiting significant activity, was further purified by a combination of silica gel column chromatography and high-performance liquid chromatography (HPLC) to afford four known glycosides (**5**—**8**). Another fraction, exhibiting insignificant activity, was acetylated and purified by silica gel column chromatography to afford a new glycoside (**9**) and three known compounds (**10**—**12**) as acetates (**9a** and **10a**—**12a**). Among the isolates tested, three compounds (**5**—**7**) exhibited significant antifeeding activities toward yellow butterfly larvae, as presented in Table I.

The antifeeding-active (**5**—**7**) and inactive compounds (**8**) were identified, by comparison of physical and spectral data with published values for the compounds themselves and/or their acetates, as osmundalin,[2] parasorboside,[3] methyl (3*S*,5*S*)-5-hydroxy-3-(β-D-glucopyranosyloxy)hexanoate,[3] and maltol β-D-glucopyranoside,[4] respectively. The other known compounds (**11** and **12**) were identified, by direct comparison of their acetates with authentic specimens, as 5-hydroxymethylfurfural and glycerin, respectively. Based on the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra (Tables II and IV) and the

TABLE I. Feeding-Inhibitory Activities of Some Isolates

Sample	Concentration (%)	Feeding ratio (%)
5	0.2	17.5
	0.1	28.4
	0.025	75.8
6	0.2	44.6
	0.1	50.0
	0.05	78.8
7	0.4	26.9
8	0.80	67.6

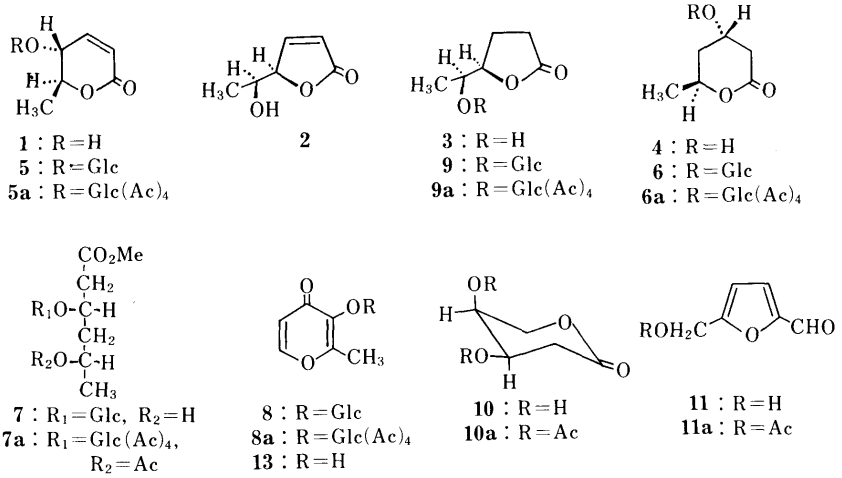

Chart 1

TABLE II. ^{1}H-NMR Chemical Shifts and Coupling Constants of O-Acetylglucosides in $CDCl_3$

Position	5a δ ppm		5a J_{H-H} Hz	6a δ ppm		6a J_{H-H} Hz	7a δ ppm		7a J_{H-H} Hz	9a δ ppm		9a J_{H-H} Hz	10a δ ppm		10a J_{H-H} Hz
2	6.05	dd	10.0 (3) 1.8 (4)	2.69 α	dbr d	17.8 (2β) 3.4 (3)	2.51	d	6.2 (3)	2.46	m		2.62 α	dd	18.9 (2β) 2.8 (3)
				2.59 β	dd	17.8 (2α) 4.2 (3)							2.99 β	dd	18.9 (2α) 7.3 (3)
3	6.74	dd	10.0 (2) 2.4 (4)	4.29	dtd	4.2 (2β) 3.4 (2α, 4α) 3.0 (4β)	4.18	m		2.20	m		5.27	dt	7.3 (2β) 2.8 (2α, 4)
4	4.29	ddd	8.5 (5) 2.4 (3) 1.8 (2)	2.18 α	ddbr d	14.5 (4β) 3.4 (3) 3.0 (5α)	2.16	m		4.38	ddd	8.2 (3) 4.6 (3) 2.3 (5)	4.67	td	3.5 (5α, 5β) 2.8 (3)
				1.69 β	ddd	14.5 (4α) 11.5 (5α) 3.0 (3)									
5	4.44	dq	8.5 (4) 6.2 (6)	4.72	dqd	11.5 (4β) 6.1 (6) 3.0 (4α)	4.18	m		4.04	qd	6.6 (6) 2.3 (4)	4.28	dd	12.1 (5) 3.5 (4)
													4.38	dd	12.1 (5) 3.5 (4)
6	1.46	d	6.2 (5)	1.38	d	6.1 (5)	1.24	d	6.3 (5)	1.26	d	6.6 (5)			
COOMe							3.69	s							
1′	4.69	d	8.2 (2′)	4.59	d	8.0 (2′)	4.63	d	7.8 (2′)	4.62	d	8.1 (2′)			
2′	4.99	dd	9.4 (3′) 8.1 (1′)	4.98	dd	9.6 (3′) 8.0 (1′)	4.91	dd	9.7 (3′) 7.8 (1′)	4.99	dd	9.4 (3′) 8.1 (1′)			
3′	5.18	t	9.4 (2′, 4′)	5.19	t	9.6 (2′, 4′)	5.18	t	9.7 (2′, 4′)	5.18	t	9.4 (2′, 4′)			
4′	5.04	t	9.4 (3′, 5′)	5.07	t	9.6 (3′, 5′)	5.04	t	9.7 (3′, 5′)	5.04	t	9.4 (3′, 5′)			
5′	3.69	ddd	9.4 (4′) 5.4 (6′) 2.1 (6′)	3.70	ddd	9.6 (4′) 4.7 (6′) 2.7 (6′)	3.72	m		3.69	ddd	9.4 (4′) 5.4 (6′) 2.1 (6′)			
6′	4.16	dd	12.0 (6′) 2.1 (5′)	4.16	dd	12.7 (6′) 2.7 (5′)	4.18	m		4.16	dd	12.0 (6′) 2.1 (5′)			
	4.24	dd	12.0 (6′) 5.4 (5′)	4.23	dd	12.7 (6′) 4.5 (5′)				4.24	dd	12.0 (6′) 5.4 (5′)			
Ac	2.01	s		2.01	s		1.99	s		1.99	s		2.10	s	
	2.04	s		2.02	s		2.02	s		2.03	s		2.12	s	
	2.05	s		2.03	s		2.02	s		2.05	s				
	2.09	s		2.09	s		2.10	s		2.08	s				
							2.10	s							

Figures in parentheses indicate a proton coupling with that in question.

optical rotation, **10a** was presumed to be the acetate of 2-deoxy-L-ribopyranolactone (**10**). 2-Deoxy-L-ribonolactone has been synthesized from 2-deoxy-L-ribose.[5] Though spectral evidence has not been provided to decide whether the synthetic material is a pyrano- or a furanolactone, it is most probable that it is the same compound as **10**. This is the first isolation of **6**—**8** and **10**—**12** from *O. japonica*. However, **7** and **11** may be artifacts.[3,6] Since the ^{1}H-NMR spectra of **5**—**7** and **5a**—**7a** had not been analyzed in detail and also their ^{13}C-NMR spectra had not been reported, their signals were assigned as shown in Tables II—IV.

Compound **9**, designated dihydroisoosmundalin, was characterized as its oily tetraacetate (**9a**), $C_{20}H_{28}O_{12}$ [FAB-MS *m/z*: 461 ($M^+ + 1$)]. In the ^{1}H-NMR spectrum, **9a** exhibited signals of one *sec*-methyl group at δ 1.26 ppm, two methylene protons at δ 2.20 and 2.46 ppm coupled to each other, and two oxy-bearing methine protons at δ 4.04 and 4.38 ppm, besides the signals due to tetra-*O*-acetylglucopyranose (Table II). The splitting pattern of the ^{1}H-NMR signals due to the aglycone moiety and the observation of the carbonyl carbon signal (δ 177.09 ppm) due to a γ-lactone (Table IV) suggested that the aglycone is 5-hydroxyhexan-4-olide. Acid hydrolysis of **9a** gave **3** as an aglycone besides glucose. Based on this evidence, the structures of the acetate and its original glycoside were elucidated as **9a** and **9**, respectively.

Experimental

Instruments Ultraviolet (UV) and infrared (IR) spectra were recorded with a Hitachi 124 spectrophotometer and a Perkin Elmer 1720X FT-IR spectrometer, respectively. Other spectral measurements and HPLC were carried out with the instruments described in the previous paper.[7] DCC was conducted according to the procedure reported previously.[1]

Bioassay Procedure The feeding-inhibitory activities of the fractions and the pure samples were evaluated on the basis of the feeding ratio (FR) which was obtained according to the procedure described in the previous paper.[1] A feeding ratio of less than 50% with 0.8% test material was regarded as indicating significant activity.

Extraction and Fractionation The dried whole plants (260 g) of *O. japonica* were successively extracted with hexane, ether and MeOH (each 3.5 l × 3). The MeOH extract (44.4 g) was partitioned between $CHCl_3$ and water. The water-soluble fraction (41.98 g) was subjected to DCC using $CHCl_3$–MeOH–H_2O (5 : 5.7 : 3) mixture. The antifeeding-active fraction (F-1, 4.34 g, FR 48.5% with 0.8% test material) was chromatographed on a silica gel column to afford two fractions (F-2, 294 mg, and F-3, 730 mg), eluted with 3% and 4% MeOH in $CHCl_3$, respectively. F-3 (FR 39.6% with 0.8% test material) was again chromatographed on a silica gel column with 20% MeOH in $CHCl_3$ to give an active fraction (F-4, 225 mg, FR 22.3% with 0.8% test material). F-4 was subjected to HPLC with 10% CH_3CN in H_2O, giving two fractions (F-5, 25.5 mg and F-6, 105.9 mg) and **7** (12.2 mg). F-5 and F-6 were subjected to HPLC with 5% and 8% CH_3CN in H_2O, respectively, to afford **6** (12.6 mg), and **5** (64 mg) and **8** (27.3 mg). F-2 was acetylated in the usual way and repeatedly chromatographed on a silica gel column using 10% hexane in $CHCl_3$ as the eluent to give **11a**

TABLE III. ^{1}H-NMR Chemical Shifts and Coupling Constants of Glucosides in CD_3OD

Position	5			6			7		
	δ ppm		J_{H-H} Hz	δ ppm		J_{H-H} Hz	δ ppm		J_{H-H} Hz
2	6.03	dd	10.0 (3)	2.78 α	ddd	17.8 (2β)	2.60 (A)	dd	15.6 (2B)
			1.1 (4)			3.0 (3)			6.0 (3)
						1.1 (4α)			
				2.71 β	dd	17.8 (2α)	2.67 (B)	dd	15.6 (2A)
						4.2 (3)			6.8 (3)
3	7.10	dd	10.0 (2)	4.32	dtd	4.2 (2β)	4.28	tt	6.8 (4B, 2B)
			2.8 (4)			3.0 (2α, 4α)			6.0 (4A, 2A)
						2.8 (4β)			
4	4.49	ddd	6.3 (5)	2.27 α	dtd	14.2 (4β)	1.61 (A)	ddd	13.8 (4B)
			2.8 (3)			3.0 (3, 5)			6.0 (3)
			1.1 (2)			1.1 (2α)			5.0 (5)
				1.74 β	ddd	14.2 (4α)	1.87 (B)	ddd	13.8 (4A)
						11.4 (5)			7.8 (5)
						2.8 (3)			6.8 (3)
5	4.59	quintet	6.3 (4, 6)	4.88	dqd	11.4 (4β)	3.94	dqd	7.8 (4B)
						6.2 (6)			6.2 (6)
						3.0 (4α)			5.0 (4A)
6	1.46	d	6.3 (5)	1.35	d	6.2 (5)	1.18	d	6.2 (5)
COOMe							3.68	s	
1′	4.50	d	7.9 (2′)	4.37	d	7.9 (2′)	4.39	d	7.9 (2′)
2′	3.21	dd	8.5 (3′)	3.16	dd	8.9 (3′)	3.12	dd	9.1 (3′)
			7.9 (1′)			7.9 (1′)			7.9 (1′)
3′	3.40	t	8.5 (2′, 4′)	3.35	t	8.9 (2′, 4′)	3.34	t	9.1 (2′, 4′)
4′	3.32	t	8.5 (3′, 5′)	3.28	t	8.9 (3′, 5′)	3.28	t	9.1 (3′, 5′)
5′	3.38	m		3.30	m		3.29	m	
6′	3.67	dd	11.2 (6′)	3.64	dd	10.0 (6′)	3.65	dd	11.8 (6′)
			4.9 (5′)			5.0 (5′)			5.5 (5′)
	3.88	br d	11.2 (6′)	3.85	dd	10.0 (6′)	3.86	dd	11.8 (6′)
						2.0 (5′)			1.4 (5′)

Figures in parentheses indicate a proton coupling with that in question.

TABLE IV. ^{13}C-NMR Chemical Shifts (δ ppm) of **3**, **5**—**7**, **5a**—**7a**, **9a** and **10a**

Position	3	5[a)]	6[a)]	7[a)]	5a	6a	7a	9a	10a
1	177.75	165.15	173.23	173.82	162.30	168.96	171.27	177.09	173.74
2	28.63	121.62	36.46	40.64	121.95	35.21	39.67	28.08	34.83
3	20.96	147.78	72.16	75.74	144.41	70.32	74.29	20.82	71.12
4	83.59	73.40	36.84	45.39	73.03	35.98	41.26	81.91	82.05
5	67.41	79.34	74.97	66.26	77.13	72.72	67.94	78.09	63.33
6	17.70	18.63	21.67	23.71	18.16	21.39	20.06	17.59	
COOMe				52.24			51.70		
1′		102.85	103.74	103.78	98.94	99.17	100.65	102.00	
2′		74.86	74.77	75.14	71.15	70.95	71.31	71.32	
3′		77.97	78.00	78.02	72.58	72.50	72.88	72.86	
4′		71.55	71.61	71.71	68.25	68.32	68.63	68.54	
5′		78.21	78.00	78.02	72.16	72.08	71.71	71.71	
6′		62.77	62.78	62.91	61.81	61.85	62.13	62.07	
$\underline{C}H_3CO$					20.54 (2C)	20.51	20.59 (3C)	20.57 (2C)	20.63
					20.70	20.57 (2C)	20.71	20.69	20.73
					20.78	20.71	21.35	20.82	
$CH_3\underline{C}O$					169.13	169.33 (2C)	169.30	169.50	170.04
					169.33	170.15	169.41 (2C)	169.89	170.31
					170.20	170.48	170.33	170.08	
					170.45		170.63	170.61	

a) These compounds were measured in CD_3OD and others in $CDCl_3$.

(7.5 mg), **10a** (32.0 mg) and **9a** (40.9 mg).

Osmundalin (5) A colorless powder, mp 104—105 °C (MeOH), $[\alpha]_D^{20}$ −107° (c=1.0, MeOH). FAB-MS m/z: 291 (M^++1). IR ν_{max}^{KBr} cm^{-1}: 3369 (OH), 1736, 1711 (CO), 1630 (C=C).

Acetylation of **5** with Ac_2O–pyridine reagent followed by chromatography on silica gel and elution with $CHCl_3$ yielded tetra-*O*-acetylosmundalin (**5a**) as colorless needles, mp 172—175 °C (MeOH), $[\alpha]_D^{20}$ −40.9° (c=0.9, $CHCl_3$). EI-MS m/z: 459 (M^++1). IR ν_{max}^{KBr} cm^{-1}: 1752, 1722 (CO), 1635 (C=C).

Parasorboside (6) Colorless needles, mp 143—145 °C (H_2O–acetone), $[\alpha]_D^{20}$ −20° (c=1, H_2O). EI-MS m/z: 293 (M^++1). IR ν_{max}^{KBr} cm^{-1}: 3422 (OH), 1720 (CO).

Acetylation of **6** in the usual way gave tetra-*O*-acetylparasorboside (**6a**) as colorless needles, mp 154—157 °C (MeOH), $[\alpha]_D^{20}$ −19° (c=2.62, $CHCl_3$). EI-MS m/z: 461 (M^++1). IR ν_{max}^{KBr} cm^{-1}: 1748 (CO).

Methyl (3*S*,5*S*)-5-Hydroxy-3-(β-D-glucopyranosyloxy)hexanoate (7) A colorless syrup, $[\alpha]_D^{20}$ −27.4° (c=0.43, MeOH). FAB-MS m/z: 325 (M^++1).

Acetylation of **7** in the usual way afforded a pentaacetate (**7a**) as colorless needless, mp 72—75 °C (ether–petroleum ether), $[\alpha]_D^{20}$ −10° (c=

1.1, $CHCl_3$). EI-MS *m/z*: 535 ($M^+ + 1$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1749 (CO).

Maltol β-D-Glucopyranoside (8) Colorless needles, mp 107—109 °C (AcOEt–MeOH),[8] $[\alpha]_D^{20}$ −55.8° (*c* = 1.06, MeOH). FAB-MS *m/z*: 289 ($M^+ + 1$). UV λ_{max}^{MeOH} nm (log ε): 211 (4.08), 257 (4.08). IR ν_{max}^{KBr} cm^{-1}: 3491 (OH), 1660, 1648 (CO), 1627, 1570 (C=C).

Acetylation of **8** in the usual way gave a tetraacetate (**8a**) as colorless needles, mp 117—119 °C (hexane), $[\alpha]_D^{20}$ −37.5° (*c* = 0.94, $CHCl_3$). FD-MS *m/z*: 457 ($M^+ + 1$). UV λ_{max}^{MeOH} nm (log ε): 211 (3.73), 255 (3.69). IR ν_{max}^{KBr} cm^{-1}: 1757, 1657 (CO), 1623, 1573 (C=C). ^{1}H-NMR ($CDCl_3$) δ ppm: 2.31 (3H, s, 2-CH_3), 6.34 (1H, d, *J* = 5.4 Hz, 5-H), 7.63 (1H, d, *J* = 5.4 Hz, 6-H), 2.02 (3H, s, OAc), 2.03 (3H, s, OAc), 2.04 (3H, s, OAc), 2.14 (3H, s, OAc), 3.65 (1H, ddd, *J* = 10.0, 4.8, 2.8 Hz, 5′-H), 4.15 (1H, dd, *J* = 12.0, 2.8 Hz, 6′-H), 4.20 (1H, dd, *J* = 12.0, 4.8 Hz, 6′-H), 5.12 (1H, dd, *J* = 10.0, 9.6 Hz, 4′-H), 5.19 (1H, dd, *J* = 9.6, 7.9 Hz, 2′-H), 5.29 (1H, t, *J* = 9.6 Hz, 3′-H), 5.35 (1H, d, *J* = 7.9 Hz, 1′-H). ^{13}C-NMR ($CDCl_3$) δ ppm: 15.24 (2-CH_3), 117.35 (C-5), 141.25 (C-2), 153.73 (C-6), 161.30 (C-3), 173.60 (C-4), 20.59 ($\underline{C}H_3CO \times 2$), 20.74 ($\underline{C}H_3CO$), 20.81 ($\underline{C}H_3CO$), 61.61 (C-6′), 68.51 (C-4′), 71.37 (C-2′), 71.82 (C-5′), 72.55 (C-3′), 99.42 (C-1′), 167.30 ($CH_3\underline{C}O \times 2$), 170.03 ($CH_3\underline{C}O$), 170.42 ($CH_3\underline{C}O$).

Acid Hydrolysis of 8 Hydrolysis of **8** (18 mg) with 10% HCl gave, besides glucose, maltol (**13**) (6 mg) as colorless needles, mp 114—117 °C (hexane–acetone). HR-MS *m/z*: 126.0315 (M^+) (Calcd for $C_6H_6O_3$: 126.0316). UV λ_{max}^{MeOH} nm (log ε): 214 (4.12), 278 (3.96). IR ν_{max}^{KBr} cm^{-1}: 3270 (OH), 1656 (CO), 1626, 1562 (C=C). The resulting glucose was identified by comparison of the ^{1}H-NMR spectrum of its acetate with that of the mixture of penta-*O*-acetyl-α- and -β-D-glucopyranose formed by acetylation of D-glucose.

Tetra-*O*-acetyldihydroisoosmundalin (9a) A colorless syrup, $[\alpha]_D^{20}$ −9.8° (*c* = 1.2, $CHCl_3$). HR-MS *m/z*: 461.1653 ($M^+ + 1$) (Calcd for $C_{20}H_{29}O_{12}$: 461.1650). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1752 (CO).

Acid Hydrolysis of 9a Hydrolysis of **9a** (9.5 mg) with 10% HCl gave, besides glucose, the aglycone (**3**) (1.5 mg) as a colorless syrup, $[\alpha]_D^{20}$ −10° (*c* = 0.1, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590, 3420 (OH), 1733 (CO). Its ^{13}C-NMR data are listed in Table IV. This compound was identified by direct comparison with an authentic sample. The resulting glucose was identified by comparison of the ^{1}H-NMR spectrum of its acetate with that of the mixture of penta-*O*-acetyl-α- and -β-D-glucopyranose formed by acetylation of D-glucose.

3,4-Di-*O*-acetyl-2-deoxy-L-ribopyranolactone (10a) A colorless syrup, $[\alpha]_D^{20}$ −4.4 (*c* = 1.0, $CHCl_3$). EI-MS *m/z*: 217 ($M^+ + 1$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 (CO).

5-Acetyloxymethylfurfural (11a) A colorless syrup. EI-MS *m/z*: 168 (M^+). ^{1}H-NMR ($CDCl_3$) δ ppm: 2.15 (3H, s, OAc), 5.13 (2H, s, CH_2-O), 6.59 (d, *J* = 3.5 Hz, H-4), 7.21 (1H, d, *J* = 3.5 Hz, H-3), 9.64 (1H, s, CHO). This compound was identified by direct comparison with an authentic sample.

Tri-*O*-acetylglycerin (12a) A colorless syrup. ^{13}C-NMR ($CDCl_3$) δ ppm: 20.71 ($\underline{C}H_3CO \times 2$), 20.91 ($\underline{C}H_3CO$), 62.30 (C-1, 3), 69.13 (C-2), 170.00 ($CH_3\underline{C}O$), 170.54 ($CH_3\underline{C}O \times 2$). This compound was identified by direct comparison with an authentic sample.

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8) Though this glycoside had been isolated as a syrup previously,[4] it was crystallized in this case.