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DITERPENE AND DITERPENE GLYCOSIDES FROM *RABDOSIA ERIOCALYX*

AKIRA ISOGAI, XIAOYU SHEN, KAZUO FURIHATA,* HIDETOSHI KANIWA,† HANDONG SUN‡ and AKINORI SUZUKI§

Department of Agricultural Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan; *Institute of Applied Microbiology, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan; †Yamanouchi Pharmaceutical Co. Ltd. 1-8, Azusawa 1-chome, Itabashi-ku, Tokyo 174, Japan; ‡Kunming Institute of Botany, Academia Sinica, Kunming, Yunnan, China

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Key Word Index—*Rabdosia eriocalyx*; Labiatae; *ent*-kaurene; diterpene; diterpene glycoside; maoecrystal K; rabdoside 1; rabdoside 2.

Abstract—An *ent*-kaurene diterpenoid, maoecrystal K, and its β-glucopyranoside, rabdoside 1, as well as a minor diterpene glycoside, rabdoside 2, were isolated from *Rabdosia eriocalyx*. The structures of the three compounds were determined by their spectral properties and chemical transformations.

INTRODUCTION

A series of *ent*-kaurene diterpenoids have been isolated from *Rabdosia eriocalyx* Hara [1, 2], and, in our previous paper, we reported on the structures of maoecrystal I and J, two new diterpenoids from the ether soluble fraction of this plant [3]. Very few reports [4] have been published on the components of the polar and water-soluble fractions of *Rabdosia* species which might contain glycosidic terpenoids. In the present communication, we report the isolation and the structural elucidation of two polar components, a new *ent*-kaurene diterpenoid and two diterpene glycosides, of this plant.

RESULTS AND DISCUSSION

The butanol-soluble fraction obtained from the methanol extract of *R. eriocalyx* afforded three compounds which we have named maoecrystal K (**1**), rabdoside 1 (**2**) and rabdoside 2 (**3**).

Maoecrystal K (**1**) gave an $[M+H]^+$ ion at *m/z* 367 in FABMS, which is consistent with the molecular formula $C_{20}H_{30}O_6$. The entire carbon skeleton of maoecrystal K as an analogue of ent-7α-hydroxy-7β,20-epoxy-kaur-16-en type derivatives could be deduced by its ^1H and ^{13}C NMR spectra (Tables 1 and 2) [3, 5].

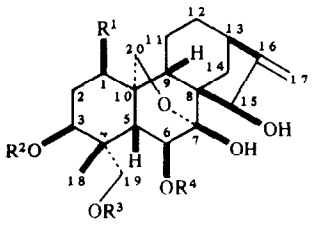
The ^1H and ^{13}C NMR data including 2D-NMR (homonuclear and heteronuclear COSY) proved the existence of hydroxyl protons including the following fragments: $-CH_2-CH_2-CH(OH)-$ and $-CH-CH(OH)-$ groups bearing quaternary carbons at both ends, and $-CH_2-OH$ and $-CH(OH)$ groups attached to quaternary carbons. The signals of an AX system, δ_H 3.76 and 1.80 (each 1H, *d*, 6.0 Hz) and δ_C 73.5 (*d*) and 53.7 (*d*), suggested that one of the hydroxyl groups was located at C-6. In addition, **1** was acetylated with acetic anhydride in pyridine to afford a triacetate (**4**). The ^1H NMR spectral data of **4** indicated that C-1 or C-3, C-6 and the oxygenated methylene at C-4 of **1** each had a hydroxyl substituent. Thus the protons at δ_H 3.85 (1H, *t*, 2.5 Hz), 3.76 (1H, *d*, 6.0 Hz), and 3.87 and 3.72 (each 1H, ABd, 11.5 Hz) in **1** showed the expected downfield shifts to δ_H 4.99 (*t*, 2.5 Hz), 5.36 (*d*, 6.0 Hz), and 4.39 and 4.50 (each 1H, ABd, 11.5 Hz) in **4**. Compound **1** showed only end absorption in its UV spectrum and no ketone carbonyl signals in its ^{13}C NMR spectrum. An allylic alcohol system, C=C–CH–OH, was deduced from the signal at δ_H 4.41 (*t*, 2.5 Hz). The assignment of the position and orientation of the allylic alcohol determined by subjecting **1** to an acid catalysed (0.1 M HCl) garryfoline–cuauchicine rearrangement [3–5]. The rearrangement product, a saturated ketone (**5**), was not produced in quantitative amounts, which means that the C-15 hydroxyl group in **1** has α-orientation. Compound **5** showed a negative Cotton effect at 255 and 295 nm, which indicated that the absolute configuration of the D ring is α [6]. Comparison of the ^{13}C–^1H COSY spectrum of **5** with that of **1** confirmed that the newly formed methyl at C-16 in **5** is α on the basis of its chemical shift: δ_C 52.5 and δ_H 2.43 (*quintet*, 6.3 Hz) [1, 6].

From the above data, the structure of **1** was determined. Its sterochemistry was proven unequivocally through chemical transformation of maoecrystal J (**6**) to **1** by treatment with lithium aluminium hydride [3, 5].

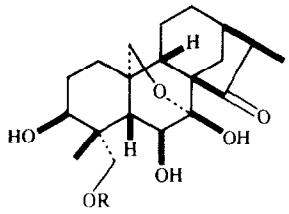
The M_r of rabdoside 1 (**2**) was determined by FABMS which gave *m/z* 529 $[M+H]^+$ and 551 $[M+Na]^+$. The ^{13}C NMR data suggested that **2** had 26 carbon atoms. The ^1H NMR and ^{13}C NMR spectral data (Tables 1 and 2), indicated that **2** has a carbon skeleton similar to maoecrystal K (**1**) and an additional hexose moiety. The Double Quantum Filtered COSY (DQF COSY) [9] (Fig. 1) and ^{13}C–^1H COSY spectra (Fig. 2) of **2** readily revealed that the structure of the aglycone of **2** was the same as that of maoecrystal K (**1**). Therefore rabdoside 1 (**2**) appeared to be a monoglycosidic *ent*-7α-hydroxyl-7β,20-epoxy-kaur-16-en derivative.

Enzymatic hydrolysis of **2** with pectolyase Y-23 (Seishin Pharmaceutical Co., No. YS-7021) gave maoecrystal K (**1**) (HPLC and the ^1H NMR). However, on acid hydrolysis with 0.1 M HCl, **2** underwent a quantitative

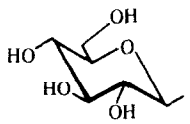
§Author to whom correspondence should be addressed.



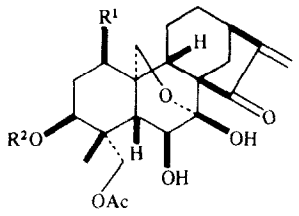
	R^1	R^2	R^3	R^4
1	H	H	H	H
2	H	H	Glc	H
3	OH	H	Glc	H
4	H	Ac	Ac	Ac
8	H	Ac	Ac-Glc	H
9	OH	H	H	H



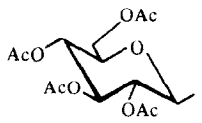
	R
5	H
7	Glc



Glc



	R^1	R^2
6	H	Ac
10	OH	H



Ac-Glc

Table 1. ^{1}H NMR data for compounds **1**–**3***

H		1		2		3
1	1.57 *m*		1.56 *m*		3.52 *t*	3.0
1	1.11 *ddd*	15.0, 3.0, 2.0	1.18 *br d*	15.0	—	
2	1.72 *ddd*	15.0, 3.0, 2.0	1.79 *m*		1.90 *ddd*	15.0, 3.0, 3.0
2	1.54 *m*		1.53 *m*		1.99 *ddd*	15.0, 3.0, 3.0
3	3.85 *t*	2.0	3.86 *br s*		3.99 *t*	3.0
5	1.80 *br d*	6.0	1.76 *d*	6.0	1.98 *d*	5.5
6	3.76 *d*	6.0	3.91 *d*	6.0	4.23 *d*	5.5
9	2.00 *dd*	12.0, 6.0	1.95 *br dd*	12.0, 6.0	2.46 *br t*	9.0
11	1.42 *dddd*	14.0, 13.0, 12.0, 6.0	1.42 *m*		1.53 *m*	
11	1.29 *ddd*	14.0, 9.0, 9.0	1.34 *m*		1.55 *m*	
12	2.06 *ddd*	13.0, 9.0, 9.0	2.20 *ddd*	14.0, 9.0, 9.0	2.19 *m*	
12	1.41 *dd*	13.0, 5.0	1.42 *m*		1.44 *m*	
13	2.56 *dd*	9.0, 5.0	2.61 *dd*	9.0, 5.0	2.58 *dd*	9.0, 5.0
14	1.63 *d*	12.0	1.66 *d*	12.0	1.66 *d*	12.0
14	1.55 *dd*	12.0, 5.0	1.52 *dd*	12.0, 5.0	1.57 *dd*	12.0, 5.0
15	4.41 *t*	2.5	4.20 *t*	3.0	4.43 *t*	2.5
17	5.03 *br s*		5.09 *d*	3.0	5.04 *d*	3.0
17	5.00 *s*		5.02 *br s*		5.00 *br s*	
18	1.16 *s*		1.21 *s*		1.26 *s*	
19	3.87 *d*	11.5	4.18 *d*	10.0	4.14 *d*	10.5
19	3.72 *d*	11.5	3.71 *d*	10.0	3.66 *d*	10.5
20	3.91 *dd*	10.0, 1.5	3.92	overlap	3.98 *br d*	10.0
20	3.83 *dd*	10.0, 2.5	3.96 *d*	10.0	3.78 *dd*	10.0, 2.0
glc-1			4.35 *d*	8.0	4.20 *d*	8.0
glc-2			3.28 *t*	9.0	3.19 *dd*	9.0, 8.0
glc-3			3.44 *t*	9.0	3.25 *dd*	9.0, 8.0
glc-4			3.35	overlap	3.25 *m*	
glc-5			3.37 *m*		3.22 *m*	
glc-6			3.90 *dd*	12.0, 1.5	3.89 *dd*	12.0, 2.0
glc-6′			3.70 *br d*	12.0	3.66 *d*	12.0

*1 in CD_3OD (500 MHz); 2 and 3 in CD_3OD–D_2O (1 : 1) (400 MHz). The assignments of 1 and 2 are based on 2D NMR techniques; The assignment of 3 may be interchanged.

garryfoline–cuauchichicine rearrangement to give a saturated ketone glycoside (**7**). Furthermore, **7** was hydrolysed with Pectolyase Y-23 in buffer or with 1.0 M HCl in aq. methanol to afford **5**.

The sugar moiety was obtained from the enzymatic hydrolysate of **2** by column chromatography on charcoal, Dowex 50 (H^+ form) and Dowex 1 (Ac^- form), successively, and was shown to be glucose by comparison on

Table 2. ^{13}C NMR data of compounds 1–3

C	1	2	3
1	23.9	24.0	67.5
2	25.8	26.0	30.9
3	70.5	71.7	72.0
4	43.8	43.1	41.5*
5	53.7	53.6	50.0
6	73.5	73.5	73.2
7	97.9	98.0	97.5
8	52.6	52.8	52.0
9	42.7	42.8	43.0
10	36.5	36.6	43.0*
11	16.1	16.1	15.0
12	33.1	33.2	32.5
13	37.8	37.8	37.2
14	26.8	26.8	26.2
15	75.5	75.5	75.0**
16	161.7	161.8	161.2
17	107.8	107.8	107.0
18	21.9	22.7	22.0
19	67.2	75.5	74.0
20	66.2	67.1	66.0
glc-1		104.9	104.0
glc-2		75.5	74.9**
glc-3		77.9	77.8
glc-4		71.0	71.0
glc-5		78.1	78.0
glc-6		62.8	62.5

Chemical shifts (δ) in ppm relative to **1** (125 MHz, CD_3OD), **2** (100 MHz, CD_3OD-D_2O 1:1) and **3** (25 MHz, CD_3OD-D_2O 1:1).

Assignments of **1** and **2** are based on INEPT and ^{13}C–^1H correlation measurements; Assignment of **3** is based on INEPT techniques.

*,**,Assignment may be interchanged.

TLC (cellulose SF) with an authentic sample [10]. Furthermore, in the ^1H–^1H COSY and ^{13}C–^1H COSY spectra of **2**, the signals at δ_H 4.35 (*d*, 8.0) and δ_C 104.9 (*d*) are assignable to the 1-position of glucose, thus suggesting the β-configuration at the anomeric centre of the glucoside [11]. The signals of **2** at δ_C 104.9, 75.5, 77.9, 71.0, 78.1, 62.8 and at δ_H 4.35 (*d*, 8.0 Hz, anomeric proton), 3.28 (*t*, 9.0 Hz), 3.44 (*t*, 9.0 Hz), 3.55 (overlapping), 3.37 (*m*), 3.90 (*d*, 12.0 Hz) and 3.70 (*dd*, 12.0, 1.5 Hz) were in agreement with those of β-glucopyranoside [11–13].

Comparison of the ^{13}C NMR spectra data of **1** and **2** (Tables 1 and 2), indicated a glycosylation shift for C-19, C-4 and C-3, which demonstrated that the 19-hydroxyl group of **2** was glycosylated [12, 13]. This was verified by following facts: the hydroxyl methine protons at δ_H 3.87 and 3.72 (each 1H, *d*, 11.0 Hz) in **1** are shifted slightly to δ_H 4.18 and 3.71 (each 1H, *d*, 10.0 Hz) in **2**, while the chemical shifts of the latter protons remained unchanged at δ_H 4.27 and 3.74 (each 1H, *d*, 10.0 Hz) in the pentaacetate of **2** (**8**). Based on these results, the structure of **2** was established as ent-19-(β-D-glucopyransyl)-3α,6α,7α,15α-tetrahydroxy-7β,20-epoxy-kaur-16-en (**2**).

The M_r of rabdoside 2 (**3**) was determined from the $[M+Na]^+$ ion (*m/z* 567) obtained in FABMS. The ^1H NMR and ^{13}C NMR (Tables 1 and 2) also revealed the signals of a carbon skeleton of an *ent*-kaurene diterpene and the presence of an additional hexose moiety. On enzymatic hydrolysis with Pectolyase Y-23 in buffer, **3** gave glucose and an aglycone (**9**). The M_r of **9** was determined by FDMS [*m/z* 383 $[M+H]^+$]. Comparison of the ^1H NMR data of **9** with those of **1** confirmed that these two compounds have the same structure except that C-1 of **9** is substituted by a hydroxyl group. This is shown by the singlet in **9** which occurs at δ_H (400 MHz, CD_3OD): 3.52 (1-H, *t*, 3.0 Hz) and 1.92, 1.91 (2-H_2, each 1H, *ddd*, 15.0, 3.0, 3.0 Hz). The aglycone **9**, a new *ent*-kaurene diterpene, was identical with the authentic sample derived from maoecrystal I (**1**) by reduction with lithium aluminium hydride. The glucose unit has the β-configuration, as demonstrated by the NMR signals at δ_H 4.20 (*d*, 8.0 Hz) and 104.0 (*d*) for β-glucopyranoside [11–13]. Consequently it was evident that in compound **3**, glucose is linked to the hydroxyl at C-19 as in **2**: the hydroxyl methine protons resonating at δ_H 3.80 and 3.74 (each 1H, *d*, 11.0 Hz) in **9** shifted to δ_H 4.17 and 3.66 m (each 1H, *d*, 10.5 Hz) in **3**. Thus rabdoside **2** was characterized as ent-19-(β-D-glucopyransyl)-1α,3α,6α,7α,15α-penta-hydroxyl-7β,20-epoxy-kaur-16-en (**3**).

It is known that glycosides are widely distributed in higher plants. In the *Rabdosia* genus, however, little is known about the distribution and the most suitable methods for the isolation of diterpene glycosides. Isobe *et al.* [2] successfully isolated diterpene glycosides from *R. shikokiana* var. *shikokiana* using DCCC. Our separation methods are useful because the columns used clearly separated the diterpene glycosides which were detectable by ^{13}C NMR. The distribution of *ent*-kaurene diterpene glycoside in the *Rabdosia* genus is not clear from a chemotaxonomic view. The presence of glycosides is not accidental, even if glycosidic components are not found in abundance in this genus. Fujita *et al.* [3] have reviewed the chemistry and the physiological activity of *ent*-kaurene diterpenoids from the *Rabdosia* genus. Their data indicate that the physiological activity of *ent*-kaurene diterpene glycosides should be tested.

EXPERIMENTAL

Mps: uncorr. ^1H and ^{13}C NMR: JNM FX-100, JOEL JNM GX-400 or JOEL JNM GX-500; HPLC: ODS C_{18} (4 × 250 mm).

Extraction and isolation. Dried and finely powdered leaves of *R. eriocalyx* (Dunn) Hara (8.0 kg), collected on Oct. 1985 at Yanzhonghai, Yunnan, China, were extracted with MeOH (5 × 3 l) at room temp. for 20 days. Filtration and evapn of the solvent gave 880 g of the residue. The residue was partitioned between EtOAc and H_2O, and the aq. soln was extracted with *n*-BuOH. The *n*-BuOH soln was evapd *in vacuo* to yield 80 g of brown gum. 43 g of the gum was suspended in 300 ml H_2O and subjected to CC over activated charcoal (320 ml). The column was eluted with H_2O, Me_2CO–H_2O (5, 10, 30, 40, 50 and 80%), successively. The 30% fraction (4.8 g) was then subjected to a Sephadex LH-20 (65 g) column eluted with 50% MeOH–H_2O to yield 3.0 g (Frs 8–14), which was further purified on a column of silanized silica gel 60 (45 g) eluted with 30% MeOH–H_2O to yield five fractions. Fr. 1 (0.18 g) and Fr. 2 (0.95 g) were purified successively on Lobar Lichroprep RP-8 (type B) eluted with 0.1% TFA in 50% MeOH and on Lobar Lichroprep Si 60 (type B) eluted with $CHCl_3$–MeOH–H_2O (35:15:1) to give 45 mg of **1**, 167 mg of **2** and 48 mg of crude **3**, respectively. Finally, 26 mg of pure **3** was obtained by HPLC using an ODS_{18} column eluted with 40% MeOH.

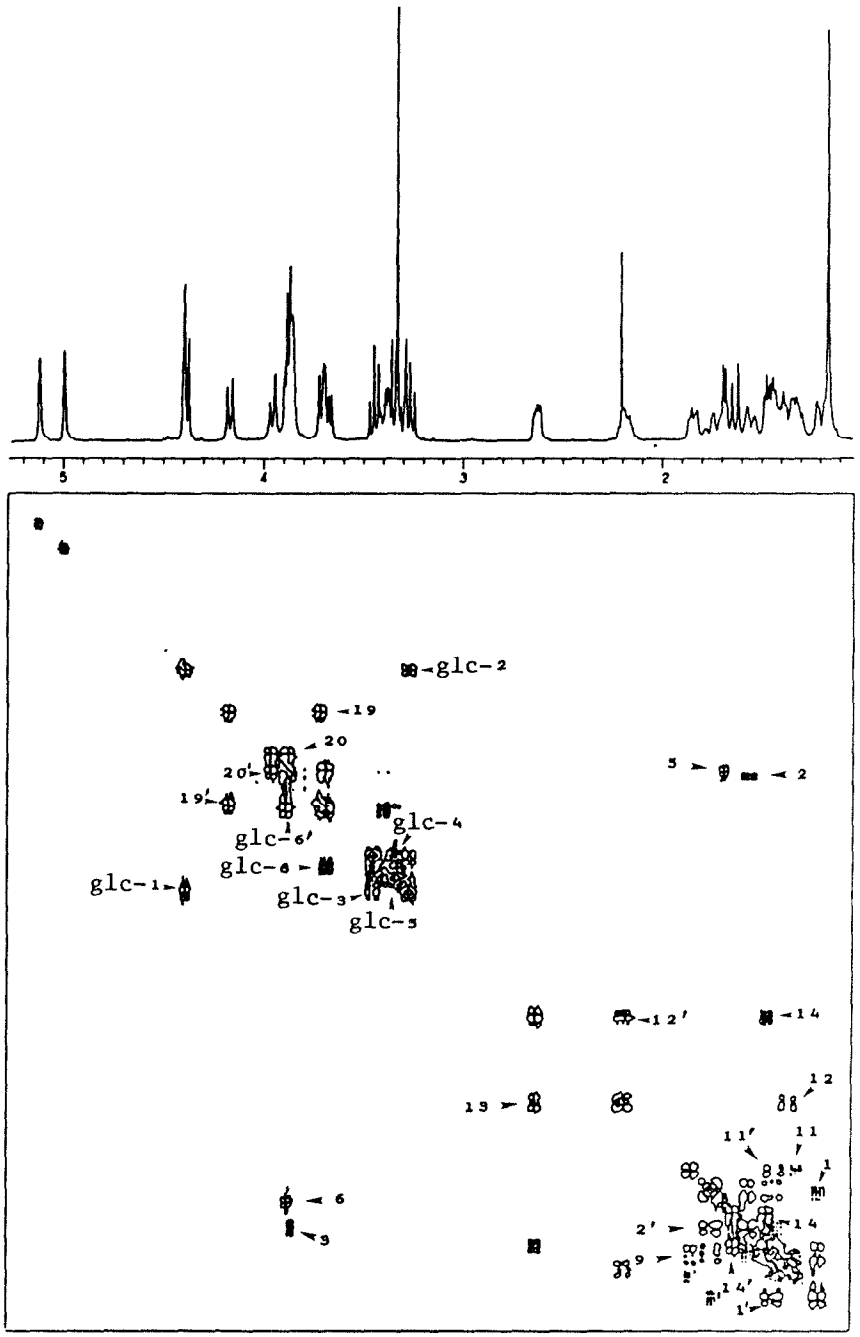


Fig. 1. Double quantum filtered COSY spectrum of rabdoside 1 (**2**) (400 MHz, CD_3OD–D_2O)

Maoecrystal K (**1**). Mp 191.5–193°; $[\alpha]_D^{26.5} = -1.3$ (MeOH; *c* 1.0); FABMS *m/z*: 367 $[M+H]^+$, 389 $[M+Na]^+$; UV (MeOH): end absorption; IR $^{Nujol}_{max}$ cm^{-1}: 3350, 3180, 1640, 1450, 1030; ^1H and ^{13}C NMR: see Tables 1 and 2.

Rabdoside 1 (**2**). Mp 179–180°; $[\alpha]_D^{26.5} = -4.6$ (MeOH; *c* 1.0); FABMS *m/z*: 529 $[M+H]^+$, 551 $[M+Na]^+$ and 567 $[M+K]^+$; UV (MeOH): end absorption; IR $^{Nujol}_{max}$ cm^{-1} 3600–3100, 2890, 1650, 1455, 1378, 1070, 1025, 1010; ^1H and ^{13}C NMR: see Tables 1 and 2.

Rabdoside 2 (**3**). Mp 170–171°; $[\alpha]_D^{26.5} = -4.5$ (MeOH; *c* 1.0); FABMS *m/z*: 567 $[M+Na]^+$; UV (MeOH): end absorption; IR $^{Nujol}_{max}$ cm^{-1}: 3650–3100, 2805, 1660, 1440, 1370, 1080–1010; ^1H and ^{13}C NMR: see Tables 1 and 2.

Triacetate of **1** (**4**). A mixture of **1** (6 mg), Ac_2O (0.3 ml) and pyridine (0.6 ml) was stirred overnight at room temp., then the reaction mixture was poured into acidic ice-water, and absorbed on to a SEP-PAK C_{18}. The column was eluted with MeOH to give **4** (4 mg). EIMS 70 eV *m/z* (rel. int.): 492 $[M]^+$ (10), 432 $[M-AcOH]^+$ (30), 372 $[M-2\times AcOH]^+$ (63) and 312 $[M-3\times AcOH]^+$ (33); δ_H (CD_3OD, 400 MHz): 1.28 and 1.69 (H_2-1, each 1H, overlap), 1.30 and 1.70 (H_2-2, each 1H, overlap), 4.99 (H-3, *t*, 3.0), 2.08 (H-5, overlap), 5.36 (H-6, *d*, 6.0), 1.52 (H-9, *dd*,

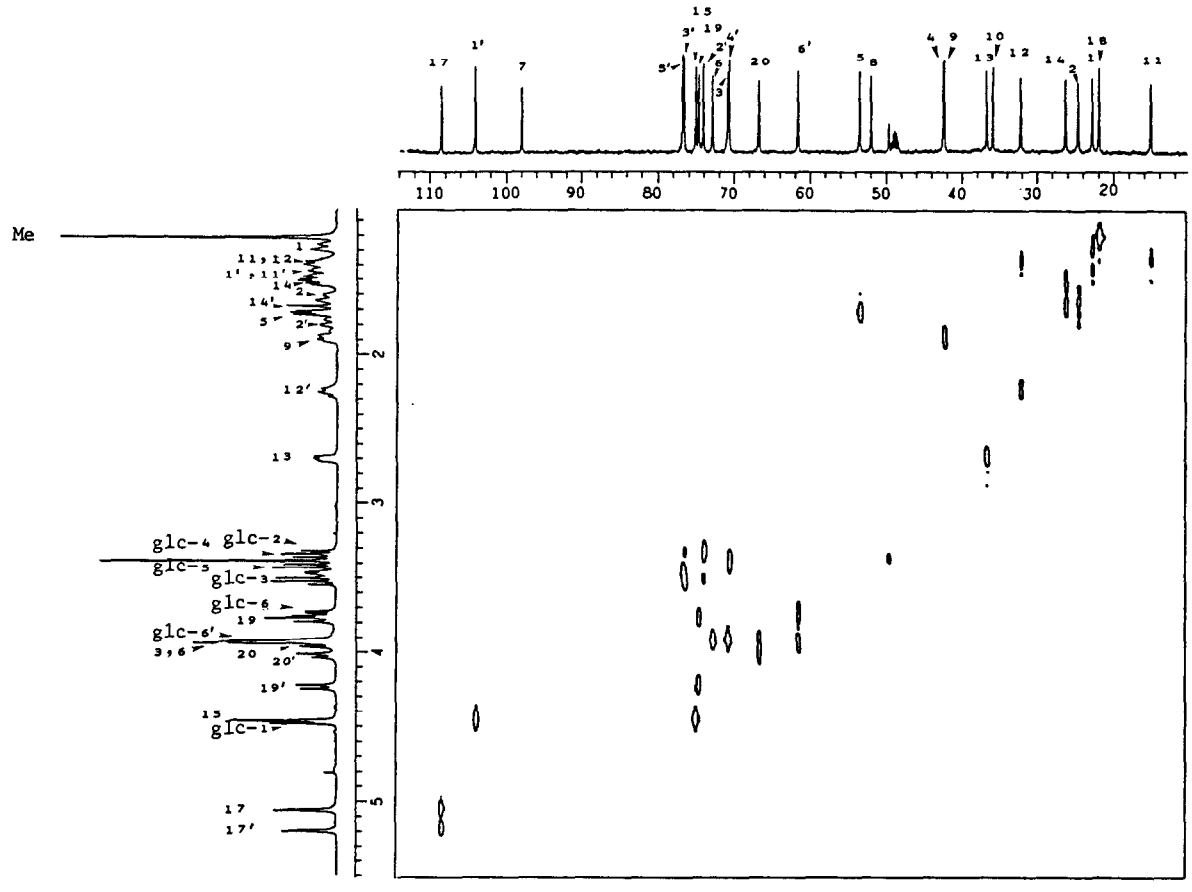


Fig. 2. ^{13}C-^{1}H COSY spectrum of rabdoside 1 (**2**) (400 MHz, CD_3OD–D_2O)

12.0, 5.0), 1.70 and 1.30 (H_2-11, overlap), 2.18 (H-12, *m*), 1.44 (H-12, *ddd*, 12.0, 12.0, 5.0), 2.56 (H-13, *dd*, 10.0, 5.0), 1.70 (H_a-14, *d*, 12.0), 1.56 (H_b-14, *dd*, 12.0, 5.0), 4.41 (H-15, *t*, 2.5), 5.06 and 5.07 (H_2-17, each 1H, *t*, 1.0), 0.95 (Me-18, 3H, *s*), 4.39 and 4.50 (H_2-19, each 1H, *d*, 11.5), 4.01 (H_a-20, *br d*, 10.0) and 3.96 (H_b–20, *dd*, 10.0, 1.5).

Rearrangement of **1** *to* **5** *with* HCl. Compound **1** (12 mg) was dissolved in MeOH (3 ml), 0.2 M HCl (3 ml) added to the soln, and the mixture stirred for 40 hr at room temp. After being poured into 20 ml of H_2O, the reaction mixture was absorbed on to a SEP-PAK C_{18}. The column was eluted with MeOH and the solvent was evapd to give a residue which was purified by HPLC using an ODS_{18} column and 40% MeOH to afford **5** (10 mg). FABMS *m/z*: 367 $[M+H]^+$ and 389 $[M+Na]^+$; ^1H NMR and ^{13}C NMR chemical shifts were assigned by the ^1H–^{13}C COSY spectrum of **5**. δ_H (CD_3OD, 400 MHz): 1.09 and 1.48 (H_2-1, each 1H, overlap), 1.55 (H-2, *m*), 1.73 (H-2, *ddd*, 15.0, 3.0, 3.0), 3.86 (H-3, *br s*), 1.80 (H-5, *d*, 6.0), 3.73 (H-6, *d*, 6.0), 1.46 (H-9, overlap), 1.62 (H-11, *ddd*, 14.0, 13.0, 12.0), 1.34 (H-11, *ddd*, 14.0, 9.0, 9.0), 1.44 and 1.83 (H_2-12, overlap), 2.52 (H-13, *br d*, 9.0), 2.19 (H_a-14, *d*, 12.0), 2.08 (H_b-14, *dd*, 12.0, 5.0), 2.42 (H-16, *quintet*, 6.3), 1.08 (Me-17, 3H, *d*, 6.3), 1.09 (Me-18, 3H, *s*), 3.87 and 3.71 (H_2-19, each 1H, *d*, 11.5) and 3.90 as well as 3.85 (H_2-20, each 1H, *d*, 10.0); δ_C (CD_3OD, 100 MHz): 22.5 (C-1, *t*), 25.7 (C-2, *t*), 70.3 (C-3, *d*), 44.0 (C-4, *s*), 57.0 (C-5, *d*), 73.9 (C-6, *d*), 96.2 (C-7, *s*) 61.3 (C-8, *s*), 51.8 (C-9, *d*), 36.6 (C-10, *s*), 17.2 (C-11, *t*), 20.0 (C-12, *t*), 32.8 (C-13, *d*), 29.0 (C-14, *t*), 227.4 (C-15, *s*), 52.1 (C-16, *d*), 10.5 (C-17, *q*), 22.0 (C-18, *q*), 67.0 (C-19, *t*) and 66.0 (C-20, *t*). CD curve (MeOH) $[\theta]_{255}$ −6600 and $[\theta]_{293}$ −8100.

Reduction of maoecrystal J (**6**) *with* $LiAlH_4$. Compound **6** (89 mg, 0.2 mol) was dissolved in dry tetrahydrofuran (3 ml), and a suspension of $LiAlH_4$ (30 mg, 0.8 mol) in Et_2O (30 ml) was added to the soln under stirring. The mixture was stirred for 1.5 hr at room temp., after which time H_2O (10 ml) was added and the organic solvent evapd *in vacuo*. The aq. soln was extracted (×3) with 20 ml *n*-BuOH saturated with H_2O. The BuOH phases were combined, dried and evapd to give a residue (60 mg). A part of the residue (5 mg) was purified by HPLC using an ODS C_{18} column and 40% MeOH to give **1** (3 mg) which was identical with an authentic sample of **1** (HPLC and 400 MHz ^1H NMR).

Enzymatic hydrolysis of **2**. Compound **2** (30 mg) was dissolved in 30 ml 0.2 M HOAc–NaOAc, pH 5.0, and incubated with Pectolyase Y-23 (30 mg, manufactured by Seishin Pharmaceutical Co. Ltd., No. YS-7021) at 37° for 22 hr. The reaction mixture was absorbed on to a SEP-PAK C_{18} and the column was eluted with MeOH to give a product (21 mg) which was purified by HPLC using an ODS_{18} column and 40% MeOH. This compound was found to be identical with an authentic sample of **1** [HPLC and ^1H NMR (CD_3OD, 400 MHz)].

The aq. part from the enzymatic hydrolysate of **2** was subjected to CC (10 × 1.4 cm) over activated charcoal (2 ml), Dowex 50 (H^+ form, 10 ml) and Dowex 1 (Ac^- form, 2 ml) and washed with H_2O at each step, successively, to give a light yellow powder

(9 mg) after freeze-drying. On cellulose SF TLC (10 × 10 cm) developed with EtOAc–pyridine–H_2O (upper phase, 2:1:2), only one spot, corresponding to glucose, was obtained after spraying 10% *p*-anisidine–phthalic acid in EtOH and heating for 10 min at 100°.

Rearrangement of **2** *with* HCl. The mixture of **2** (30 mg) and 0.1 M HCl in aq. MeOH (15 ml) was worked-up in the same way as that described for the rearrangement of **1** to give a saturated ketone glycoside (**7**). δ_H (CD_3OD, 400 MHz): 1.09 and 1.48 (H_2-1, each 1H, overlap), 1.55 and 1.73 (H_2-2, each 1H, overlap), 3.81 (H-3, *br s*), 1.79 (H-5, *br d*, 6.0), 3.87 (H-6, *d*, 6.0), 1.46 (H-9, overlap), 1.62 (H-11, *ddd*, 14.0, 13.0, 12.0), 1.34 (H-11, *ddd*, 14.0, 9.0, 9.0), 1.44 and 1.83 (H_2-12, overlap), 2.52 (H-13, *br d*, 9.0), 2.19 (H_a-14, *d*, 12.0), 2.06 (H_b-14, *dd*, 12.0, 5.0), 2.42 (H-16, *quintet*, 6.3), 1.07 (Me-17, 3H, *d*, 6.3), 1.26 (Me-18, 3H, *s*), 4.14 and 3.65 (H_2-19, each 1H, *d*, 11.5), 3.90 *and* 3.88 (H_2-20, each 1H, *d*, *br d*, 10.0), 4.24 (anomeric proton, *d*, 8.0), 3.21 (2′-H, *t*, 9.0), 3.86 (6′-H, *br d*, 12.0) and 3.67 (6″-H, overlap). The ^{13}C NMR chemical shifts was assigned by means of an INEPT experiment. δ_C (CD_3OD, 100 MHz): 22.7 (C-1, *t*), 25.8 (C-2, *t*), 71.7 (C-3, *d*), 43.2 (C-4, *s*), 52.2 (C-5, *d*), 73.7 (C-6, *d*), 96.2 (C-7, *s*), 61.1 (C-8, *s*), 51.5 (C-9, *d*), 37.0 (C-10, *s*), 17.1 (C-11, *t*), 28.9 (C-12, *t*), 32.8 (C-13, *d*), 19..9 (C-14, *t*), 227.4 (C-15, *s*), 56.7 (C-16, *d*), 10.6 (C-17, *q*), 22.6 (C-18, *q*), 74.6 (C-19, *t*), 67.5 (C-20, *t*), 104.8 (anomeric carbon, *d*), 75.2 (H-2′, *d*), 77.9 (C-3′, *d*), 70.9 (C-4′, *d*), 78.1 (C-5′, *d*) and 62.7 (C-6′, *t*).

Enzymatic hydrolysis of **7**. A mixture of **7** (3 mg), 6 ml of 0.2 M HOAc–NaOAc, pH 5.0, and 3 mg of Pectolyase Y-23 was incubated for 40 hr at 37° followed by the usual work-up (see above) to yield **5** (1.5 mg).

Acidic hydrolysis of **7**. Compound **7** (4 mg) was hydrolysed with 1 M HCl in aq. MeOH (15 ml) under reflux for 8 hr, then the mixture was worked by the same procedure as that described for the rearrangement of **1** to give **5** (2 mg).

Pentaacetate of **2** (**8**). A mixture of **2** (30 mg), Ac_2O (2.5 ml) and pyridine (3.0 ml), was stirred overnight at room temp. and the reaction mixture was worked-up in the usual way. The product was purified on a Lobar Lichroprep Si 60 column (type A) and eluted by C_6H_6–Me_2CO (4:1) to give **8** (28 mg). Mp 121–122°; $[\alpha]_D^{26.5} = -1.6$ ($CHCl_3$, *c* 1.0); IR_{max}^{Nujol} cm^{-1}: 3400, 1750, 1640, 1450, 1380, 1220, 1140; FABMS *m/z* 761 $[M+Na]^+$; δ_H ($CDCl_3$, 500 MHz): 1.68 and 1.73 (H_2-1, overlap), 1.36 and 1.80 (H_2-2, overlap), 5.10 (H-3, *br s*), 2.07 (H-5, overlap), 3.80 (H-6, *d*, 6.0), 2.12 and 1.40 (H_2-11, *m*), 2.62 (H-13, *br d*, 9.0), 1.72 (H_a-14, *d*, 12.0), 1.57 (H_b-14, *dd*, 12.0, 5.0), 4.45 (H-15, *br s*), 5.01 (H_2-17, *br s*), 0.95 (Me-18, 3H, *s*), 4.04 and 3.90 (H_2-19, each 1H, *d*, 11.0), 4.01 and 3.98 (H_2-20, each 1H, *d*, 10.0), 4.77 (anomeric proton, *d*, 8.0), 4.98 (H-2′, *t*, 9.0), 5.10 (H-3′, *t*, 9.0), 5.32 (H-4′, *t*, 9.0), 5.10 (H-5′, *m*), 4.35 and 4.27 (H_2-6′, *m*). The ^{13}C NMR chemical shifts were assigned by means of an INEPT experiment. δ_C ($CDCl_3$, 100 MHz): 23.0 (C-1, *t*), 24.5 (C-2, *t*), 72.4 (C-3, *d*), 42.0 (C-4, *s*), 51.9 (C-5, *d*), 73.1 (C-6, *d*), 96.8 (C-7, *s*), 52.8 (C-8, *s*), 43.1 (C-9, *d*), 36.5 (C-10, *s*), 16.0 (C-11, *t*), 32.5 (C-12, *t*), 37.5 (C-13, *d*), 27.1 (C-14, *t*), 75.0 (C-15, *d*), 161.8 (C-16, *s*), 108.9 (C-17, *t*), 21.5 (C-18, *q*), 73.5 (C-19, *t*), 67.2 (C-20, *t*), 102.0 (anomeric carbon, *d*), 72.8 (C-2′, *d*), 70.0 (C-3′, *d*), 72.8 (C-4′, *d*), 73.5 (C-5′, *d*) and 63.0 (C-6′, *t*).

Enzymatic hydrolysis of **3**. A mixture of **3** (6 mg), 12 ml of 0.2 M HOAc–NaOAc, pH 5.0, and 6 mg of Pectolyase Y-23 was incubated for 40 hr at 37° followed by the usual work-up to give **9** (3 mg). FDMS *m/z* 383 $[M+H]^+$; δ_H (CD_3OD, 400 MHz): 3.52 (H-1, *t*, 3.0), 1.92 and 1.91 (H_2-2, each 1H, *ddd*, 15.0, 3.0, 3.0), 3.99 (H-3, *t*, 3.0), 1.99 (H-5, *br d*, 5.5), 3.81 (H-6, *d*, 5.5), 2.46 (H-9, *br t*, 9.0), 1.52 and 1.54 (H_2-11, each 1H, *m*), 2.18 and 1.43 (H_2-12, each 1H, *m*), 2.58 (H-13, *dd*, 9.0, 5.0), 1.65 (H_a-14, *d*, 12.0), 1.57 (H_b-14, *dd*, 12.0, 5.0), 4.43 (H-15, *t*, 3.0), 5.04 (H_a-17, *d*, 3.0), 5.00 (H_b-17, *t*, 1.0), 1.20 (Me-18, *s*), 3.80 and 3.74 (H_2-19, each 1H, *d*, 11.0), 3.99 and 3.66 (H_2-20, each 1H, *dd*, 10.0, 2.0).

Reduction of maoecrystal I (**10**). **10** (4 mg) was dissolved in dry tetrahydrofuran (2 ml), and a suspension of $LiAlH_4$ (2 mg) in absolute Et_2O (4 ml) was added to the soln with stirring, The mixture was worked-up by the same procedure used for the reduction of **6** to yield **9** (2 mg).

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