ARUGOMYCIN, A NEW ANTHRACYCLINE ANTIBIOTIC

II. STRUCTURAL ELUCIDATION

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The structure of arugomycin was determined by chemical degradation, and NMR and mass spectral analyses to be a new anthracycline antibiotic with arugorol (4′-*epi*-nogalarol) as the chromophore and two sugar chains comprising diginosyl-decilonitrosyl-2-deoxyfucose, and (4-*O*-fumaryl-diginosyl)-diginosyl-2-deoxyfucosyl-diginose.

In the preceding paper[1], we have reported the isolation of a new antitumor antibiotic arugomycin (AGM) produced by *Streptomyces violaceochromogenes* 1098-AV$_2$. The aglycone of AGM named arugorol (AGR)[1], is the 4′-epimer of nogalarol, the chromophore of nogalamycin. This paper describes the structure determination of AGM in detail. Preliminary communication of this work has been reported[2,3].

Results and Discussions

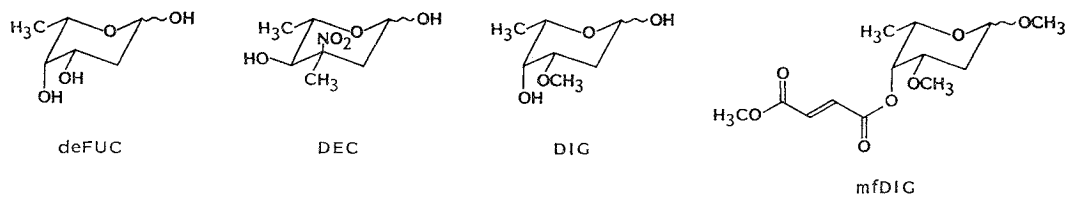
Since AGM is a very large compound with the molecular weight of *m/z* 1,694 and possesses seven sugars in its two sugar chains, the direct structure elucidation by NMR and mass spectral analyses was not feasible. Thus, NMR and mass spectral analyses of chemical degradation products were carried out by comparing with authentic samples.

Sugar Moieties

Mild acid hydrolysis of AGM in 40% formic acid gave a mixture of the aglycone and sugar moieties which was fractionated to give three sugars as anomeric mixtures. These were identified as 2-deoxy-L-fucose (deFUC)[4], L-diginose (DIG)[5], and L-decilonitrose (DEC)[5] (Fig. 1) by ^{1}H NMR spectral analyses of their free forms and acetyl derivatives, optical rotation and comparison with authentic samples.

Methanolysis of AGM gave the methyl ester of methyl 4-*O*-fumaryl-L-diginoside (mfDIG) in addi-

Fig. 1. Structures of sugar components obtained by acid hydrolysis and methanolysis of arugomycin.
deFUC: 2-Deoxy-L-fucose, DEC: L-decilonitrose, DIG: L-diginose, mfDIG: methyl fumaryl-L-diginoside.



tion to methyl glycosides of deFUC, DIG and DEC. Since the methyl ester signal (δ_H 3.81) of this compound was not observed in the ^{1}H NMR spectrum of the starting material, one of the carboxyl functions of the fumaric acid residue must be free in AGM, and 4-*O*-fumaryl-L-diginose (fDIG) must be glycosidically combined to the terminus of a sugar chain.

Partial Hydrolysis

On mild acid hydrolysis with 50% acetic acid, AGM gave a mixture of red pigments AG1, AG2, AG3 and AG4. They were separated by preparative TLC and further purified by chromatography on Toyopearl HW-40F developed with methanol. The ^{13}C NMR spectral data of these compounds are summarized in Table 1. Their structures (see Fig. 2) were determined as explained below.

AG1

Hydrolysis of AG1 with 40% aqueous formic acid at 85°C for 40 minutes gave AGR[1], deFUC and DEC. In the ^{1}H NMR spectrum of AG1, two anomeric proton signals were observed

Table 1. 100 MHz ^{13}C NMR spectral data of arugomycin and its degradation products.

Carbon	AGR	AG1	AG3	AG2	(T_1[a])	AG6	AG4	AGM	ref
1	147.5	147.8	147.6	147.5	(—)	147.7	147.6	147.9	
2	138.6	139.6	139.4	139.4	(0.89)	139.4	139.4	140.1	
3	123.8	122.1	121.7	121.8	(0.18)	121.8	121.7	122.3	
4	157.0	155.8	155.5	156.2	(1.75)	155.9	155.5	156.6	
4a	115.7	114.3	114.1	114.7	(1.41)	114.6	114.2	115.3	
5	191.1	190.5	190.1	190.9	(—)	190.9	190.0	191.8	
5a	114.5	113.8	113.8	114.2	(1.24)	112.6	113.2	114.8	
6	161.4	159.7	161.2	161.8	(2.51)	159.8	161.4	162.2	
6a	133.4	132.6	131.3	131.5	(1.67)	131.2	131.2	131.2	
7	63.8	63.9	71.4	71.4	(0.29)	21.0	71.2	70.6	
8	40.9	41.6	41.5	41.2	(0.14)	33.4	41.0	39.9	
9	70.5	70.5	70.4	70.5	(—)	70.5	70.7	69.3	
10	59.0	56.3	56.7	56.5	(0.28)	55.8	55.6	59.0	
10a	143.8	141.7	142.5	143.0	(1.36)	141.8	142.5	144.4	
11	120.3	119.0	118.3	119.0	(0.25)	119.2	119.0	119.8	
11a	133.9	133.4	132.8	133.4	(2.57)	133.0	132.8	131.2	
12	180.1	179.1	178.7	179.8	(—)	179.1	178.9	180.3	
12a	117.8	116.3	116.4	117.0	(3.09)	116.6	116.4	117.8	
13	30.1	29.1	29.1	28.9	(—)	28.9	29.3	30.0	
COO	172.3	172.5	171.9	172.4	(3.84)	173.0	171.7	171.9	
OCH_3	52.9	52.9	52.8	52.7	(0.87)	52.9	52.7	52.0	
1′	97.5	97.4	97.1	97.0	(0.23)	97.4	97.3	97.9	
2′	67.4	67.0	68.2	68.5	(0.24)	68.8	68.5	67.4	
3′	64.7	61.5	61.4	62.1	(0.25)	61.5	61.3	62.5	
4′	73.2	81.4	81.3	81.0	(0.29)	81.6	81.3	81.6	
5′	77.5	77.3	77.8	77.7	(—)	77.2	77.5	77.6	
6′	22.6	24.0	24.2	23.8	(0.13)	24.0	24.2	23.6	
NCH_3	43.1	44.5	44.4	44.1	(—)	44.7	44.3	44.3	
S1 deFUC									deFUC[4]
1		99.1	99.2	99.5	(0.32)	99.6	99.4	100.0	99.1
2		33.7	33.6	33.7	(0.20)	33.9	33.7	34.6	33.0
3		64.6	64.5	64.6	(0.23)	64.0	64.6	65.0	65.9
4		82.6	82.6	82.7	(0.26)	82.9	82.5	82.3	71.6
5		68.8	66.9	67.1	(—)	67.5	67.9	67.9	68.4
6		17.1	17.1	16.6	(0.61)	17.0	16.8	17.1	17.9

Table 1. (Continued)

Carbon	AGR	AG1	AG3	AG2	(T_1[a])	AG6	AG4	AGM	ref
S2 DEC									DEC[6]
1		99.3	99.2	99.6	(0.36)	99.1	99.2	99.7	98.6
2		41.6	41.5	41.8	(0.24)	42.1	41.8	41.9	41.7
3		89.4	89.2	88.7	(2.62)	88.7	88.5	89.5	88.6
4		76.1	76.7	83.8	(0.45)	83.9	83.6	83.6	77.0
5		71.4	71.4	70.3	(—)	69.0	70.3	70.6	71.1
6		18.6	18.5	18.6	(0.59)	19.0	18.8	18.6	18.3
CH_3		25.2	25.2	25.1	(0.53)	25.4	25.2	24.9	25.2
S3 DIG									DIG[6]
1				101.7	(0.43)	101.6	101.4	102.3	98.7
2				30.0	(0.22)	30.3	30.9	(30.9)	29.4
3				74.1	(0.41)	74.2	74.4	(75.4)	74.8
4				67.3	(0.43)	67.2	67.3	67.5	67.8
5				67.1	(—)	66.9	67.3	67.2	65.5
6				16.8	(—)	17.3	17.0	(17.3)	16.8
OCH_3				55.6	(—)	55.8	56.3	56.1	54.8
S4 DIG									
1			100.9	101.0	(0.33)		100.7	102.1	
2			29.7	29.6	(0.13)		30.1	31.9	
3			74.9	74.9	(0.27)		74.1	74.9	
4			68.2	68.1	(0.34)		75.3	(75.9)	
5			66.9	66.6	(0.37)		67.9	(68.3)	
6			17.1	16.8	(—)		17.6	(17.6)	
OCH_3			55.8	55.6	(—)		56.2	56.1	
S5 deFUC									
1							99.2	100.0	
2							32.4	(34.4)	
3							65.8	65.8	
4							67.9	81.1	
5							67.3	67.4	
6							17.6	17.2	
S6 DIG									
1								100.4	
2								(31.9)	
3								(74.9)	
4								(75.3)	
5								(68.3)	
6								(17.6)	
OCH_3								(56.1)	
S7 fDIG									
1								100.0	
2								(31.7)	
3								(73.8)	
4								(72.3)	
5								(65.4)	
6								(17.6)	
OCH_3								(55.9)	
CH=								139.3	
CH=								134.3	
COOH								168.9	
OCO								166.0	

The spectra were obtained in $CDCl_3$, except for AGM (in pyridine-d_5) and AGR (in CD_3OD). Similar values in parentheses may be interchanged.

[a] Longitudinal relaxation time of AG2 in second.

as doublets at δ_H 5.36 (1-H, S1†) and δ_H 4.68 (1-H, S2).

The anomeric carbons were observed at δ_C 99.1 (C-1 of S1) and 99.3 (C-1 of S2). This result indicated that AG1 consists of one mol each of AGR, deFUC and DEC. Comparison of the ^{13}C NMR data of AG1 and AGR revealed the glycosidation shift of C-4′ (δ_C 73.2 in AGR vs. 81.4 in AG1) but not of C-7 (δ_C 63.8 vs. 63.9) and C-2′ (δ_C 67.4 vs. 67.0) in the aglycone part of AG1. This evidence suggested the attachment of the carbohydrate moiety only to C-4′ of the chromophore. A similar glycosidation shift was observed with C-4 of deFUC(S1) from δ_C 71.6 to 82.6[6]. These ^{13}C chemical shifts indicated that DEC is attached to C-4 of the deFUC(S1) moiety.

The secondary ion mass spectrometry (SI-MS) spectrum of AG1 showed the protonated fragmentation peaks at *m/z* 586, 700 and 716 due to the cleavages as sketched in Fig. 2. The coupling constants of the anomeric protons of deFUC(S1) and DEC(S2) were $J_{1,2ax}$=2.0 Hz and $J_{1,2eq} \leqq 1$ Hz, and $J_{1,2ax}$= 11.4 Hz and $J_{1,2eq} \leqq 1$ Hz, respectively. Thus the glycosidic linkages of deFUC(S1) and DEC(S2) were determined to be α and β, respectively. From the above mentioned results, the total structure of AG1 was determined to be L-decilonitrosyl-2-deoxy-L-fucosylarugorol as shown in Fig. 2.

AG3

Hydrolysis of AG3 gave DIG in addition to the components of AG1, *i.e.*, AGR, deFUC and DEC. The ^1H and ^{13}C NMR spectra of AG3 showed three signals of anomeric protons at δ_H 4.74, 5.32 and 5.46, and anomeric carbons at δ_C 99.2, 99.2 and 100.9. Therefore, AG3 contains one more DIG moiety than AG1. Comparison of the ^{13}C NMR data of AG3 and AG1 revealed the glycosidation shift of C-7 in the aglycone part of AG3 from δ_C 63.9 to 71.4. This downfield shift is reasonably explained by positioning DIG at C-7 of AG1 (see Fig. 2).

The SI-MS spectrum of AG3 showed the protonated molecular ion peak at *m/z* 1,034 $(MH)^+$ and fragment ion peaks at *m/z* 730, 858 and 873. These peaks originated from the cleavages of the linkages between the aglycone and deFUC(S1), deFUC(S1) and DEC(S2), and aglycone and DIG(S4), respectively, as shown in Fig. 2. The anomeric configuration of DIG(S4) was shown to be α. [1-H of DIG(S4), $J_{1,2ax}$=2.0 Hz and $J_{1,2eq} \leqq 1$ Hz].

AG2

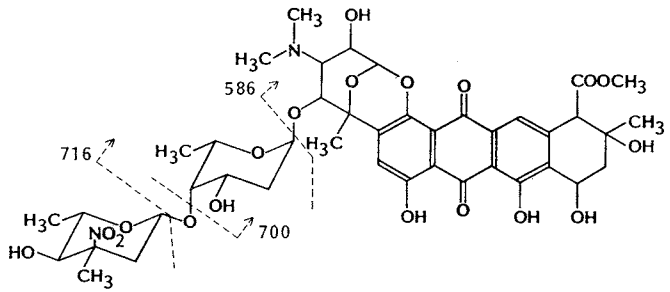
The SI-MS spectrum of AG2 gave the protonated molecular ion peak at *m/z* 1,178 (MH^+) and fragment peaks at *m/z* 1,033 and 730, the latter was also observed in the spectrum of AG3. However, the fragment peak at *m/z* 873 in AG3 was shifted to 1,017 in AG2. The ^1H and ^{13}C NMR spectra of AG2 revealed four anomeric proton signals at δ_H 4.98, 5.27, 5.33 and 5.48, and four anomeric carbons at δ_C 99.5, 99.6, 101.0 and 101.7. These results revealed that AG2 consisted of one mol each of AGR, deFUC, and DEC, and two mol of DIG. Consequently, AG2 is a monodiginosyl derivative of AG3. Comparison of the ^{13}C NMR data of AG2 and AG3 (Table 1) revealed the glycosidation shift of C-4 of DEC(S2) from δ_C 76.7 to 83.8.

The fragment ion peaks at *m/z* 730 and 1,017 in the SI-MS spectrum of AG2 suggested that the deFUC(S1)-DEC(S2)-DIG(S3) and DIG(S4) moieties attached to C-4′ and C-7 of the aglycone, respectively.

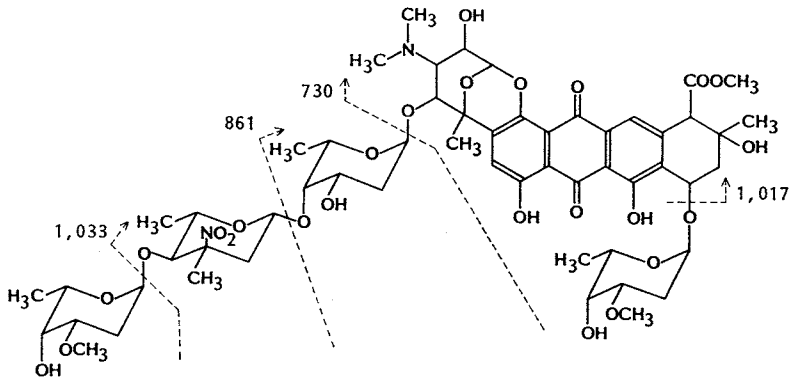
The coupling constants of the anomeric proton of DIG(S3), $J_{1,2ax}$=2.0 Hz and $J_{1,2eq}$=1 Hz, suggested the glycosidic linkage of the DIG(S3) moiety to be α. Distinction of the two DIG units in AG2 was made by assuming that longitudinal relaxation times (T_1) of S4 carbons (Table 1) would be

† "S" stands for the sugar moiety. For numbering of sugar moieties (S), see Fig. 4.

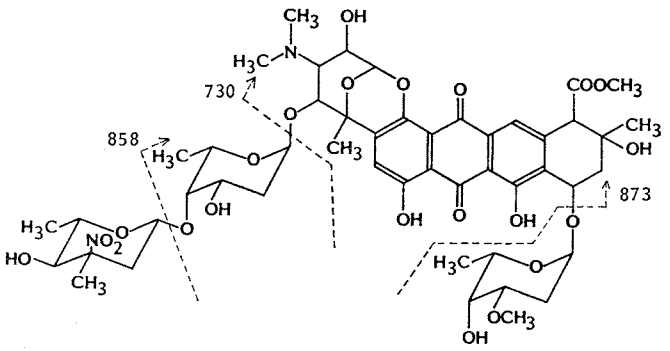
Fig. 2. SI-MS diagnostic fragment ions of AG1, AG2, AG3 and AG4.



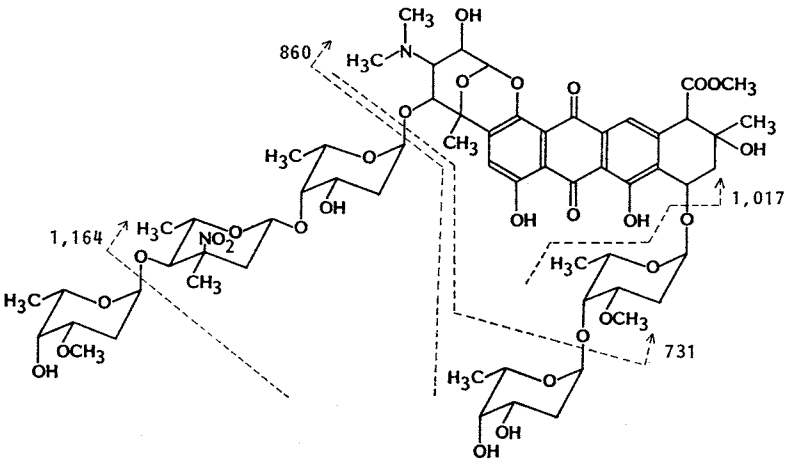
AG1
m/z 890 $(MH)^+$



AG2
m/z 1,178 $(MH)^+$



AG3
m/z 1,034 $(MH)^+$



AG4
m/z 1,308 $(MH)^+$

shorter than those of S3, since S3 was located at the terminal of the longer sugar chain linked to the C-4′ position of the aglycone.

AG4

The ^{1}H and ^{13}C NMR spectra of AG4 revealed five anomeric signals at δ_H 4.98, 5.01, 5.25, 5.32, 5.52 and δ_C 99.2, 99.2, 99.4, 100.7, 101.4, two methoxy signals due to DIG at δ_H 3.34, 3.36, and δ_C 56.2, 56.3, and one characteristic tertiary methyl signal due to DEC at δ_H 1.75 and δ_C 25.2, respectively. The SI-MS spectrum of AG4 gave the protonated molecular ion peak at *m/z* 1,308 which was larger than AG2 by 130. Since hydrolysis of AG4 gave deFUC, DIG, and DEC, this difference was assigned to the increment of one deFUC unit.

These data indicated that AG4 was a 2-deoxy-L-fucosyl derivative of AG2. Therefore, AG4 comprises AGR - DEC - deFUC - DIG in the ratio of 1 : 1 : 2 : 2. Comparison of the ^{13}C NMR spectra of AG2 and AG4 revealed the glycosidation shift of C-4 of DIG from δ_C 68.1 to 75.3 in AG4. However, since there existed two terminal DIG units (S3 and S4) with almost identical ^{13}C NMR chemical shifts in AG2, it was impossible to determine which of the terminal sugars in AG2 was glycosylated by deFUC(S5) in AG4.

This problem was solved by subjecting AG4 to hydrogenolysis with 5% Pd - $BaSO_4$, which liberates the sugar moiety in view of the benzylic nature of C-7[7]. The red residue of the reaction products was identified as 4′-(L-diginosyl-L-decilonitrosyl-2-deoxy-L-fucosyl)-7-deoxyarugorol (AG6, see later, Fig. 3) obtained by hydrogenolysis of AGM. Therefore, the additional deFUC(S5) moiety is combined to C-4 of DIG(S4) in AG2 to give the structure of AG4 as shown in Fig. 2.

This conclusion was supported by detailed analysis of the SI-MS diagnostic ions of AG4 at *m/z* 860, 1,017, 1,164 and 1,308 (see Fig. 2).

The anomeric configuration of deFUC(S5) was determined to be α, based on $J_{1,2ax}$=2.0 Hz and $J_{1,2eq} \leqq 1$ Hz.

AG6

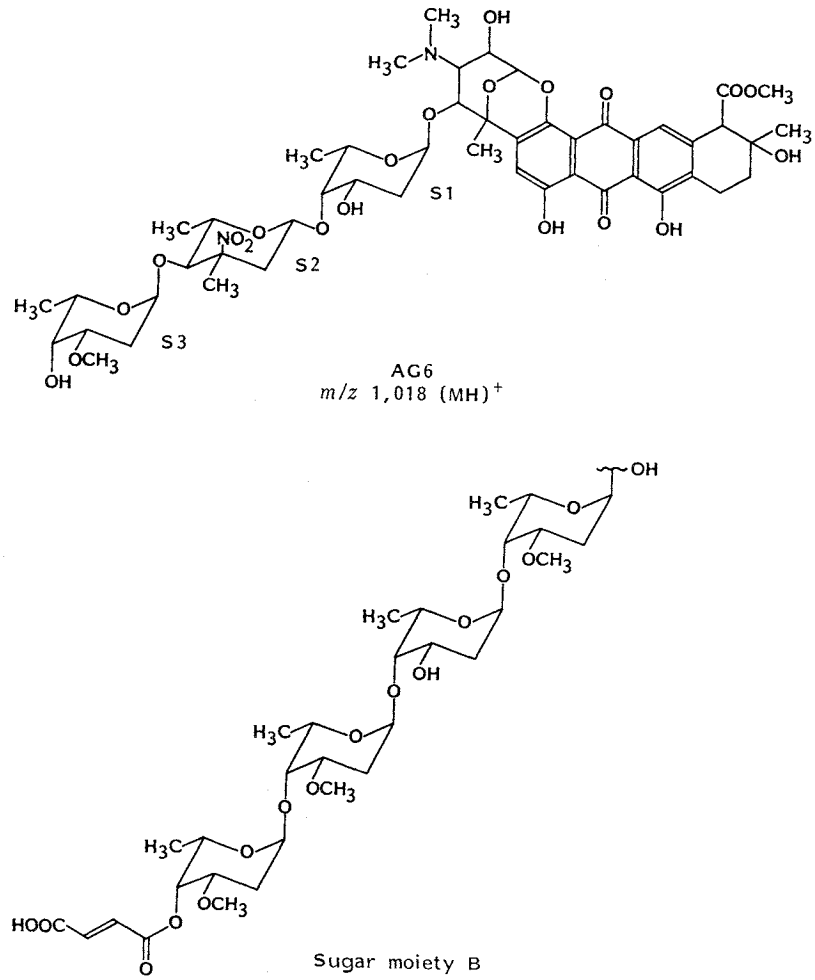
Hydrogenolysis of AGM (5% Pd - $BaSO_4$) resulted in the formation of AG6 and the sugar moiety B. The ^{13}C NMR spectrum of AG6 proved the presence of a new methylene group at δ_C 21.0 due to C-7 of the aglycone and three anomeric carbons at δ_C 99.1, 99.6 and 101.6. In accordance with this, three anomeric protons were observed at δ_H 4.97, 5.25 and 5.33 in the ^{1}H NMR spectrum of AG6. The SI-MS spectrum of AG6 showed the molecular ion peak at *m/z* 1,018. These spectral data indicated that AG6 consisted of three sugars and 7-deoxy-AGR. Since the sugar linkage to C-4′ of the aglycone had been established in AG2, the structure of AG6 was also established (Fig. 3).

Sugar Moiety B

The IR spectrum of the sugar moiety B gave absorptions at 2400~2800 and 1720 cm^{-1}.

The ^{1}H NMR spectrum of the sugar moiety B was obtained with an anomeric mixture which proved the presence of four sugars [δ_H 4.76 (dd, J=10.4 and 2.0 Hz, due to β-form), 5.42 (dd, J=2.0 and <1 Hz, α-form), 4.97 (dd, J=2.0 and <1 Hz), 4.99 (dd, J=2.0 and <1 Hz), 5.05 (dd, J=2.0 and <1.0 Hz)] and three methoxy groups (δ_H 3.36, 3.41 and 3.42) due to DIG. Furthermore, the spectrum showed a characteristic AB-type quartet at δ_H 6.80 and 6.90 (J=17.0 Hz) arising from a fumaric acid half ester residue. These data indicated that the sugar moiety B consisted of one mol each of fumaric acid and deFUC and three mol of DIG. Since the linkage of deFUC(S5)-DIG(S4) and C-7 of arugorol had been established in AG4, the sugar moiety B was 4-*O*-fumaryl-DIG(S7)-DIG(S6)-

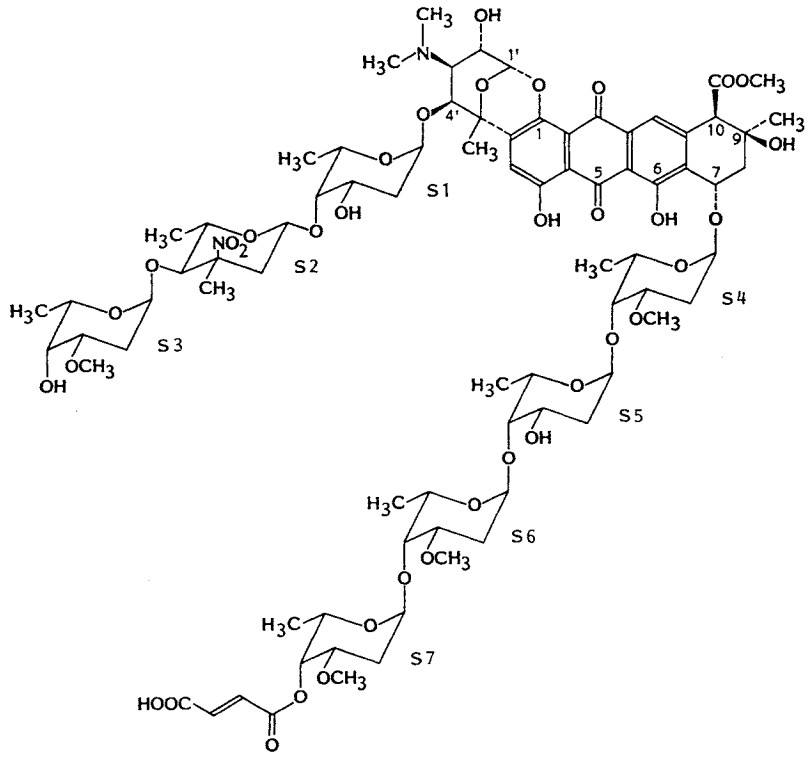
Fig. 3. Structures of hydrogenolysis products of arugomycin.



deFUC(S5)-DIG(S4).

The unsettled question at this point was to establish the position of the free hydroxy group in deFUC(S5). Treatment of the sugar moiety B with acetic anhydride in pyridine gave an anomeric mixture of diacetates. Since the separation of these anomers was very difficult, the diacetates were analyzed without further separation. In the ^{1}H NMR spectrum, two acylated proton signals were observed at δ_H 6.24 and 5.67 (the total area of these anomeric proton signals being equal to 1H), and 5.21. Irradiation of the proton at δ_H 5.21 changed the methylene signal (ddd) at δ_H 1.95 and 2.10 to a doublet of doublets, and thus the free hydroxy group was unambiguously assigned to C-3 of deFUC. Therefore, the fumaryl-DIG(S7)-DIG(S6) unit must be attached to deFUC(S5) through an α-1,4 linkage. The sequence of the sugar residues in the structure of sugar moiety B was thus determined to be 4-*O*-fumaryl-L-diginosyl-L-diginosyl-2-deoxy-L-fucosyl-L-diginose as shown in Fig. 3. Based on these experimental results, the total structure of AGM can be represented as shown in Fig. 4.

Fig. 4. Structure of arugomycin.



Materials and Methods

General

NMR spectra were recorded on a Jeol GX400 spectrometer, UV spectra were determined on a Shimadzu UV-300 and IR spectra on a Jasco A-102 spectrophotometer (KBr pellets or $CHCl_3$). Melting points were determined on a Yanagimoto micro melting point apparatus and were not corrected. Optical rotations were measured with a Jasco DIP-4. The SI-MS spectra were taken by a Hitachi M-80A using diethanolamine as a matrix.

Hydrolysis of AGM

A solution of AGM (200 mg) in 3 ml of 40% formic acid was heated in an oil bath at 85°C for 40 minutes. The reaction mixture diluted with water (50 ml) was applied to a Diaion HP-20 column (4×10 cm) and after being washed with water, the column was developed with methanol. The eluate was concentrated to dryness *in vacuo* to give a red residue which was separated by preparative silica gel TLC with chloroform - methanol (4 : 1). A red band with Rf 0.3 was eluted with chloroform - methanol (1 : 1) and the eluate was evaporated. The red solid thus obtained was gel-filtered on a Sephadex LH-20 column (4×70 cm) to give pure AGR as a solid (42 mg).

The effluent of the Diaion HP-20 column was neutralized with 4 N NaOH and evaporated. Silica gel TLC analysis of the residue with chloroform - methanol (9 : 1) showed the mixture to contain three components (Rf 0.2, 0.4 and 0.45). This mixture was dissolved in chloroform - methanol (50 : 1), and chromatographed on a silica gel column (3×40 cm) with chloroform - methanol (50 : 1). Each fraction (10 ml) was checked by TLC with the above mentioned conditions and tubes which gave same Rf value were pooled. The first fraction (Rf 0.45) contained decilonitrose (8 mg), and the second fraction (Rf 0.4) contained diginose (40 mg). The following eluate with chloroform - methanol (10 : 1) contained 2-deoxyfucose (12 mg).

A solution of decilonitrose (4 mg) in 5% methanolic hydrogen chloride was heated at 60°C for 1 hour and the reaction mixture was evaporated. The residue was dissolved in chloroform and chromatographed on a silica gel column (1×20 cm) with chloroform. The main fraction contained methyl β-L-decilonitroside (3 mg), which was identified by comparison with an authentic sample.

Methyl β-L-Decilonitroside: Oily substance; $[\alpha]_D^{22}$ −10° (*c* 0.5, $CHCl_3$) (literature 6, $[\alpha]_D^{23}$ −13±3°); ^1H NMR δ 1.39 (3H, d, J=6.0 Hz, 6-H), 1.74 (3H, s, 3-CH_3), 1.76 (1H, dd, J=10.0 and 13.0 Hz, 2-H_a), 2.74 (1H, dd, J=1.2 and 13.0 Hz, 2-H_b), 3.08 (1H, d, J=11.0 Hz, 4-H), 3.48 (3H, s, OCH_3), 3.68 (1H, m, J=6.0 and 11.0 Hz, 5-H), 4.50 (1H, dd, J=1.0 and 10.0 Hz, 1-H); IR ($CHCl_3$) 1545, 1370 cm^{-1}.

The absolute configurations of diginose and 2-deoxyfucose were determined to be L by their optical rotation $[\alpha]_D^{22}$ −56° (*c* 0.5, water) (literature 8, $[\alpha]_D^{25}$ −64.7±5.4°) and $[\alpha]_D^{22}$ −53° (*c* 0.5, water) (literature 9, $[\alpha]_D^{14}$ −61.6±2°), respectively.

Partial Hydrolysis of AGM

A solution of AGM (200 mg) in 50% acetic acid was heated in an oil bath at 85°C for 20 minutes. The mixture was diluted with water and extracted with chloroform three times. The solvent layer was evaporated and the residue was purified by preparative silica gel TLC (chloroform - methanol, 10:1) to give a mixture of AG1 and AG3 (5.4 mg), AG2 (18.1 mg) and AG4 (12.9 mg). The AG1 and AG3 mixture was further purified on a Toyopearl HW-40F column (2×40 cm) with methanol to give AG1 (1.0 mg) and AG3 (3.2 mg).

AG1: MP 235~236°C; IR (KBr) 3430, 1740, 1620 cm^{-1}; $[\alpha]_D^{22}$ +610° (*c* 0.1, MeOH); SI-MS *m/z* 890 (MH^+); UV λ_{max}^{MeOH} nm (ε) 237 (63,100), 255 (34,700), 290 (11,600), 478 (15,200).

AG2: MP 201~203°C; IR (KBr) 3430, 1740, 1620 cm^{-1}; $[\alpha]_D^{22}$ +369° (*c* 0.1, MeOH); SI-MS *m/z* 1,178 (MH^+); UV λ_{max}^{MeOH} nm (ε) 235 (47,800), 259 (22,600), 293 (7,400), 478 (13,800).

AG3: MP 208~209°C; IR (KBr) 3430, 1740, 1620 cm^{-1}; $[\alpha]_D^{22}$ +430° (*c* 0.1, MeOH); SI-MS *m/z* 1,034 (MH^+); UV λ_{max}^{MeOH} nm (ε) 235 (47,800), 257 (22,400), 290 (8,300), 478 (14,800).

AG4: MP 209~210°C; IR (KBr) 3430, 1740, 1620 cm^{-1}; $[\alpha]_D^{22}$ +330° (*c* 0.1, MeOH); SI-MS *m/z* 1,308 (MH^+); UV λ_{max}^{MeOH} nm (ε) 235 (52,700), 257 (24,300), 290 (9,500), 478 (16,100).

Hydrogenolysis of AGM

A solution of AGM (200 mg) in chloroform - methanol (1:1) was hydrogenated over 5% Pd-$BaSO_4$ (15 mg) at room temp (2.0 kg/cm^2) for 8 hours. The reaction mixture was filtered and the filtrate evaporated to dryness. The residue was purified by preparative silica gel TLC to give AG6 (17 mg) and the sugar moiety B (8 mg).

AG6: MP 165~168°C; IR (KBr) 3430, 1740, 1620 cm^{-1}; $[\alpha]_D^{21}$ +393 (*c* 0.1, MeOH); SI-MS *m/z* 1,018 (MH^+); UV λ_{max}^{MeOH} nm (ε) 235 (54,900), 248 (28,500), 292 (11,900), 478 (16,000).

Sugar Moiety B: MP 115~118°C; $[\alpha]_D^{21}$ −93.9° (*c* 0.1, MeOH).

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