A Family of Novel Macrocyclic Lactones, the Saccharocarcins Produced by *Saccharothrix aerocolonigenes* subsp. *antibiotica*

II. Physico-chemical Properties and Structure Determination

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(Received for publication July 26, 1996)

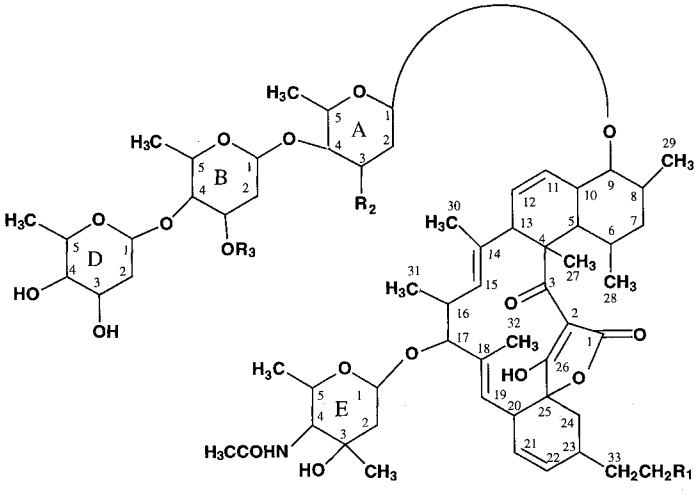
Six novel tetronic acid analogs were isolated from the fermentation broth of the actinomycete *Saccharothrix aerocolongenes* subsp. *antibiotica* SCC1886. The structures of these saccharocarcins were determined by their spectral data, and chemical degradation. All six compounds are derived from two modified tetronic acid homologs which differ from other tetronic acids by having an ethyl or propyl side chain at C-23 and a methyl group at C-16. They are all characterized by a novel sugar-amide at C-17.

In the preceding paper we have described the fermentation, isolation, antibacterial and antichlamydial activity of six novel compounds from the fermentation broth of a soil actinomycete identified as *Saccharothrix aerocolongenes* subsp. *antibiotica*. Spectroscopic studies showed these compounds to have a tetronic acid containing macrocyclic lactone structure, similar to kijanimicin[1~5], tetrocarcin[6~9] and antlermycin[10,11]. In this paper the physico-chemical properties and structure elucidation of all six compounds are presented.

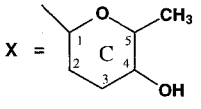
Results

The physico-chemical properties of saccharocarcins A~F (**1~6**) are summarized in the experimental section. All were isolated as white powders and the UV spectra of these compounds are similar and are indicative of tetronic acid containing macrocyclic lactone compounds. Like most of the other tetronic acid derivatives saccharocarcins are leavorotatory in nature and the specific rotation ranged for the analogs from 150~173°. IR spectra are also similar and revealed the presence of an amide (1630, 1555 cm^{-1}) and an ester (1755 cm^{-1}) functionality.

Saccharocarcin A (**1**) was isolated as a white amorphous solid, mp 220°C. The fast atom bombardment (FAB) mass spectrum displayed an intense molecular ion peak at *m/z* 1240 $(M+H)^+$ and a sodiated species at *m/z* 1262 $(M+Na)^+$ and when KCl is added, it showed an intense peak at *m/z* 1278 $(M+K)^+$ revealing the molecular weight to be 1239. Peak matching using high resolution mass measurements showed the elemental composition $C_{67}H_{101}NO_{20}$. The mass spectral fragmentation of kijanimicin (**7**) has been extensively studied.[5]

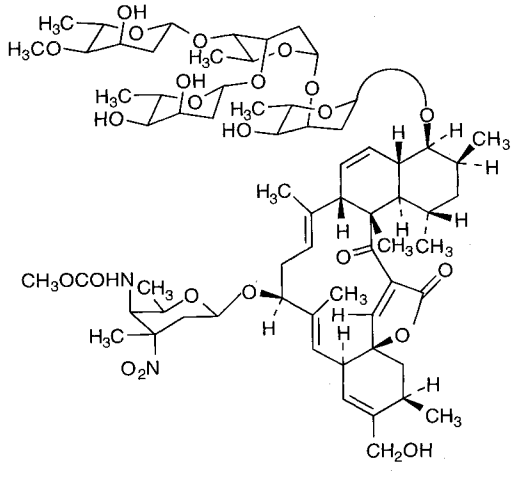


1 Saccharocarcin A R_1 = -H, R_2 = -OH, R_3 = -X
2 Saccharocarcin B R_1 = -CH_3, R_2 = -OH, R_3 = -X
3 Saccharocarcin C R_1 = -H, R_2 = -H, R_3 = -H
4 Saccharocarcin D R_1 = -H, R_2 = -H, R_3 = -X
5 Saccharocarcin E R_1 = -CH_3, R_2 = -H, R_3 = -H
6 Saccharocarcin F R_1 = -CH_3, R_2 = -H, R_3 = -X



Comparison of the fragmentation patterns of saccharocarcin A with that of **7** indicated various changes in the molecule. Saccharocarcin A is 77 mass units lower than that of **7** *m/z* 1339 $(M+Na)^+$. Comparison of the molecular formula of both indicated that **1** has equal number of carbon atoms but one nitrogen and four oxygen less than that of kijanimicin.

The structures of these compounds were determined mainly by ^1H NMR, ^{13}C NMR, COSY and mass spectral fragments. The odd molecular weight was indicative of presence of odd number of nitrogen atoms. The elemental composition also revealed eighteen degrees of unsaturation. ^1H NMR and ^{13}C NMR spectra were complex but revealed the presence of five sugars. The ^{13}C NMR (Table 1) also showed 67 carbons, confirming with the molecular formula. In the ^1H NMR spectrum of **1** in $CDCl_3$ the downfield proton signal at δ 5.92 is coupled to the proton signal at δ 5.4 and also to the proton signal at δ 3.55. These proton signals at δ 5.92 and 5.4 are linked to sp^2 carbons C-21 and C-22, respectively and the proton signal at δ 3.55 is attached to C-20. The proton signals at δ 5.74 and 5.37 are coupled to each other and in turn coupled to proton signals at δ 3.35 and 2.36. These protons are attached to C-12 and C-11, and those at δ 3.35 and 2.36 are attached to C-13 and C-10 respectively. In the ^{13}C NMR spectrum the carbon signals at 167.1 and 170.4 ppm are probably due to ester or amide carbonyl functionalities and those at 202.1 and 206.2 ppm are due to the presence of two keto functions (enolic keto at C-26 and C-3). Carbon signals in sp^2 region (118.9, 125.7, 125.8, 126.8, 130.0, 130.9, 134.5 and 138.4) and the proton carbon coupling studies [Heteroatom correlation studies (HETCOR)] revealed the presence of four double bonds. Rest of the carbon connectivities was traced by ^1H-^1H COSY, ^{13}C-^1H long range couplings and HMBC, revealed the structure of the aglycone as shown in Fig. 1. The sugar sequence was also established using ^1H-^1H COSY, ^{13}C-^1H long-range coupling studies [Selective insensitive nuclei enhancement bipolarization transfer studies (SINEPT)] as shown in Fig. 2a. The attachment of the E-sugar to the tetronic acid moiety was also established by (^{13}C-^1H) long range coupling studies as



7

Fig. 1. Long-range ^1H-^{13}C couplings observed for the aglycone in the HMBC spectrum of **1**.

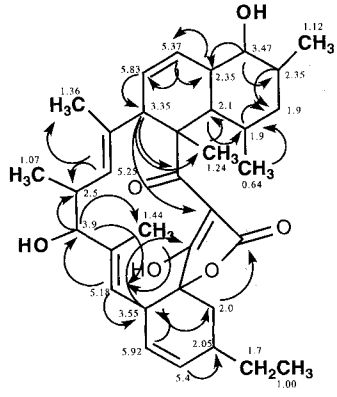
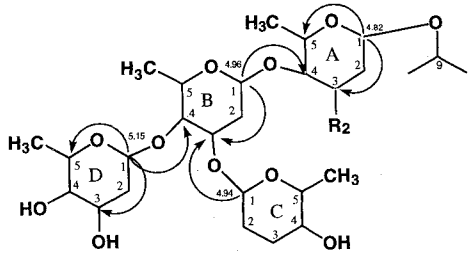
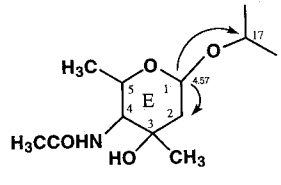


Fig. 2. Long-range ^1H-^{13}C couplings observed for the sugar sequence (SINEPT) of **1**.



4a



4b

Table 1-1. ^{13}C NMR chemical shifts of different components from the culture SCC 1886.

Carbon No.	7	1	2	3	4	5	6
C-1	167.1 (s)	167.2 (s)	167.2 (s)	167.2 (s)	167.1 (s)	167.1 (s)	167.1 (s)
C-2	109.9 (s)	101.7 (s)	101.7 (s)	101.6 (s)	101.6 (s)	101.7 (s)	101.6 (s)
C-3	206.2 (s)	206.2 (s)	206.2 (s)	206.1 (s)	206.1 (s)	206.2 (s)	206.2 (s)
C-4	51.0 (s)	50.8 (s)	50.8 (s)	50.8 (s)	50.8 (s)	50.8 (s)	50.8 (s)
C-5	31.3 (d)	31.3 (d)	31.3 (d)	31.2 (s)	31.2 (s)	31.2 (s)	31.2 (s)
C-6	27.9 (d)	27.7 (d)	27.7 (d)	27.6 (d)	27.6 (d)	27.7 (d)	27.7 (d)
C-7	41.6 (t)	41.7 (d)	41.8 (t)	41.7 (t)	41.7 (t)	41.7 (t)	41.7 (t)
C-8	38.5 (d)	34.5 (d)	34.5 (d)	34.3 (d)	34.3 (d)	34.4 (d)	34.3 (d)
C-9	84.5 (d)	84.3 (d)	84.3 (d)	83.6 (d)	83.6 (d)	83.6 (d)	83.6 (d)
C-10	34.8 (d)	38.3 (d)	38.5 (d)	38.4 (d)	38.4 (d)	38.4 (d)	38.4 (d)
C-11	125.8 (d)	125.8 (d)	125.8 (d)	125.6 (d)	125.6 (d)	125.6 (d)	125.6 (d)
C-12	126.7 (d)	126.8 (d)	126.8 (d)	126.7 (d)	126.7 (d)	126.8 (d)	126.7 (d)
C-13	53.2 (d)	53.5 (d)	53.5 (d)	53.4 (d)	53.4 (d)	53.4 (d)	53.4 (d)
C-14	135.7 (s)	134.4 (s)	134.4 (s)	134.3 (s)	134.3 (s)	134.3 (s)	134.4 (s)
C-15	123.6 (d)	130.0 (d)	130.1 (d)	129.9 (d)	129.9 (d)	129.9 (d)	129.9 (d)
C-16	31.1 (t)	35.0 (d)	32.9 (d)	34.9 (d)	34.9 (d)	32.8 (d)	32.8 (d)
C-17	78.4 (d)	83.4 (d)	83.4 (d)	83.4 (d)	83.4 (d)	83.3 (d)	83.4 (d)
C-18	137.1 (s)	138.4 (s)	138.4 (s)	138.3 (s)	138.3 (s)	138.3 (s)	138.3 (s)
C-19	121.5 (d)	125.7 (d)	125.7 (d)	125.6 (d)	125.6 (d)	125.5 (d)	125.5 (d)
C-20	43.1 (d)	43.3 (d)	43.3 (d)	43.2 (d)	43.2 (d)	43.3 (d)	43.2 (d)
C-21	119.3 (d)	118.9 (d)	118.9 (d)	118.8 (d)	118.8 (d)	118.9 (d)	118.8 (d)
C-22	141.5 (s)	130.9 (d)	131.1 (d)	130.8 (d)	130.8 (d)	131.0 (d)	131.0 (d)
C-23	40.2 (d)	39.6 (d)	39.6 (d)	39.6 (d)	39.6 (d)	39.6 (d)	39.5 (d)
C-24	35.5 (t)	34.3 (t)	34.3 (t)	35.1 (t)	35.1 (t)	35.1 (t)	35.1 (t)
C-25	83.3 (s)	82.9 (s)	82.9 (s)	82.8 (s)	82.8 (s)	82.8 (s)	82.8 (s)
C-26	201.5 (s)	202.1 (s)	202.2 (s)	202.0 (s)	202.0 (s)	202.1 (s)	202.0 (s)
C-27	20.2 (q)	18.9 (q)	19.0 (q)	18.6 (q)	18.6 (q)	18.6 (q)	18.6 (q)
C-28	22.2 (q)	22.3 (q)	22.3 (q)	22.2 (q)	22.2 (q)	22.2 (q)	22.3 (q)
C-29	14.0 (q)	14.2 (q)	14.3 (q)	14.1 (q)	14.1 (q)	14.1 (q)	14.1 (q)
C-30	15.1 (q)	15.3 (q)	17.1 (q)	15.2 (q)	15.2 (q)	15.2 (q)	15.2 (q)
C-31	13.7 (q)	15.2 (q)	15.3 (q)	15.1 (q)	15.1 (q)	15.1 (q)	15.1 (q)
C-32	64.4 (t)	13.1 (q)	13.1 (q)	13.1 (q)	13.1 (q)	13.1 (q)	13.1 (q)
C-33	15.1 (q)	28.8 (t)	38.1 (t)	28.7 (t)	28.7 (t)	38.0 (t)	38.0 (t)
C-34	—	12.7 (q)	21.1 (t)	12.6 (q)	12.6 (q)	21.1 (t)	21.1 (t)
C-35	—	—	14.1 (q)	—	—	14.0 (q)	14.0 (q)
C-1A	98.2 (d)	98.1 (d)	98.1 (d)	98.5 (d)	98.5 (d)	98.5 (d)	98.5 (d)
C-2A	29.9 (t)	29.8 (t)	29.8 (t)	22.8 (t)	22.8 (t)	22.8 (t)	22.8 (t)
C-3A	66.8 (d)	66.5 (d)	66.5 (d)	29.1 (t)	29.1 (t)	29.1 (t)	29.1 (t)
C-4A	71.8 (d)	82.3 (d)	82.3 (d)	82.4 (d)	82.5 (d)	82.5 (d)	82.5 (d)
C-5A	65.1 (d)	65.1 (d)	65.1 (d)	68.3 (d)	68.3 (d)	68.4 (d)	68.3 (d)
C-6A	17.9 (q)	17.8 (q)	18.5 (q)	18.1 (q)	18.4 (q)	18.1 (q)	18.4 (q)
C-1B	90.8 (d)	91.0 (d)	91.0 (d)	91.9 (d)	91.9 (d)	91.9 (d)	91.9 (d)
C-2B	29.7 (t)	36.9 (t)	36.9 (t)	37.8 (t)	36.7 (t)	37.8 (t)	36.7 (t)
C-3B	62.6 (d)	70.4 (d)	70.4 (d)	68.2 (d)	68.0 (d)	68.3 (d)	68.0 (d)
C-4B	79.6 (d)	75.2 (d)	75.2 (d)	74.5 (d)	75.1 (d)	74.5 (d)	75.1 (d)
C-5B	67.1 (d)	68.1 (d)	68.1 (d)	69.4 (d)	70.3 (d)	69.3 (d)	70.3 (d)
C-6B	17.9 (q)	18.1 (q)	18.1 (q)	17.7 (q)	17.7 (q)	17.7 (q)	17.7 (q)
C-1C	92.2 (d)	92.0 (d)	92.0 (d)	—	91.9 (d)	—	91.9 (d)
C-2C	34.4 (t)	27.4 (t)	27.4 (t)	—	27.4 (t)	—	27.4 (t)
C-3C	67.5 (d)	30.0 (t)	30.1 (t)	—	29.7 (t)	—	29.7 (t)
C-4C	72.4 (d)	71.9 (d)	72.0 (d)	—	71.7 (d)	—	71.7 (d)
C-5C	64.9 (d)	63.9 (d)	63.9 (d)	—	63.9 (d)	—	63.9 (d)
C-6C	17.9 (q)	17.8 (q)	18.3 (q)	—	17.7 (q)	—	17.7 (q)
C-1D	99.8 (d)	98.4 (d)	98.4 (d)	98.9 (d)	98.9 (d)	98.8 (d)	99.0 (d)
C-2D	36.8 (t)	40.3 (t)	40.3 (t)	40.2 (t)	40.2 (t)	40.3 (t)	40.2 (t)
C-3D	63.8 (d)	65.5 (d)	65.5 (d)	66.2 (d)	66.2 (d)	66.3 (d)	66.2 (d)
C-4D	82.6 (d)	71.7 (d)	71.7 (d)	72.7 (d)	74.5 (d)	72.8 (d)	74.5 (d)
C-5D	68.1 (d)	62.1 (d)	62.1 (d)	62.4 (d)	62.3 (d)	62.4 (d)	62.4 (d)
C-6D	18.4 (q)	18.5 (q)	19.0 (q)	18.4 (q)	18.8 (q)	18.4 (q)	19.8 (q)

Table 1-2. ^{13}C NMR chemical shifts of different components from the culture SCC 1886.

Carbon No.	7	1	2	3	4	5	6
C-1E	97.1 (d)	97.9 (d)	97.9 (d)	97.9 (d)	97.8 (d)	97.8 (d)	97.8 (d)
C-2E	35.7 (t)	32.3 (t)	32.7 (t)	32.3 (t)	32.3 (t)	32.7 (t)	32.6 (t)
C-3E	91.0 (s)	72.7 (s)	72.7 (s)	72.7 (s)	72.7 (s)	72.8 (s)	72.7 (s)
C-4E	53.8 (d)	55.5 (d)	55.5 (d)	55.4 (d)	55.4 (d)	55.4 (d)	55.4 (d)
C-5E	69.1 (d)	67.7 (d)	67.7 (d)	67.7 (d)	67.7 (d)	67.7 (d)	67.7 (d)
C-6E	17.0 (q)	17.1 (q)	17.9 (q)	17.0 (q)	17.0 (q)	17.0 (q)	17.0 (q)
3E-CH_3	25.3 (q)	34.1 (q)	34.1 (q)	34.0 (q)	34.0 (q)	34.1 (q)	34.0 (q)
4E-$\underline{C}OCH_3$	157.4 (s)	170.4 (s)	170.4 (s)	170.5 (s)	170.4 (s)	170.4 (s)	170.4 (s)
4E-$CO\underline{C}H_3$	52.7 (q)	23.4 (s)	23.5 (q)	23.4 (q)	23.4 (q)	23.4 (q)	23.4 (q)

Table 2. ^{13}C NMR of aglycones of kijanimicin, saccharocarcin A and B.

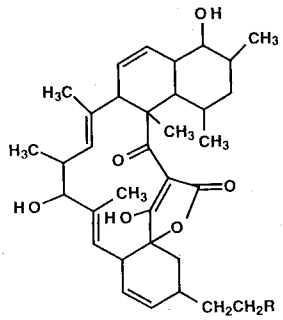
Carbon No.	13	10	11	12	8	9
C-1	167.1 (s)	167.2 (s)	167.1 (s)	177.3 (s)	167.2 (s)	167.3 (s)
C-2	102.0 (s)	101.8 (s)	101.8 (s)	100.1 (s)	102.1 (s)	102.2 (s)
C-3	206.5 (s)	206.3 (s)	206.2 (s)	203.6 (s)	206.4 (s)	206.5 (s)
C-4	51.1 (s)	50.9 (s)	50.9 (s)	52.6 (s)	50.9 (s)	51.0 (s)
C-5	31.2 (d)	31.2 (d)	31.2 (d)	32.6 (d)	34.7 (d)	32.7 (d)
C-6	28.0 (d)	27.6 (d)	27.5 (d)	28.9 (d)	31.8 (d)	31.2 (d)
C-7	41.9 (t)	41.8 (t)	41.7 (t)	43.4 (t)	41.7 (t)	41.8 (t)
C-8	39.3 (d)	39.2 (d)	39.1 (d)	40.6 (d)	39.1 (d)	39.2 (d)
C-9	76.1 (d)	76.2 (d)	76.1 (d)	77.4 (d)	77.8 (d)	77.8 (d)
C-10	34.8 (d)	34.8 (d)	34.7 (d)	36.3 (d)	34.8 (d)	34.8 (d)
C-11	125.8 (d)	125.7 (d)	125.5 (d)	126.6 (d)	125.5 (d)	125.5 (d)
C-12	126.5 (d)	126.9 (d)	126.8 (d)	128.9 (d)	126.9 (d)	127.0 (d)
C-13	53.3 (d)	53.4 (d)	53.4 (d)	53.0 (d)	53.4 (d)	53.4 (d)
C-14	135.9 (s)	134.4 (s)	134.4 (s)	138.3 (d)	134.8 (s)	134.8 (s)
C-15	123.4 (d)	130.1 (d)	130.0 (d)	124.9 (d)	130.6 (d)	130.8 (d)
C-16	31.2 (t)	35.0 (d)	34.1 (d)	33.3 (t)	34.7 (d)	34.8 (d)
C-17	78.6 (d)	83.4 (d)	83.5 (d)	74.3 (d)	76.2 (d)	76.2 (d)
C-18	137.0 (s)	138.4 (s)	138.3 (s)	140.5 (s)	141.4 (s)	141.5 (s)
C-19	121.5 (d)	125.3 (d)	125.3 (d)	122.7 (d)	125.3 (d)	125.4 (d)
C-20	42.9 (d)	42.9 (d)	42.9 (d)	45.2 (d)	42.9 (d)	43.0 (d)
C-21	119.4 (d)	118.9 (d)	118.9 (d)	120.4 (d)	117.8 (d)	117.8 (d)
C-22	141.5 (s)	130.8 (d)	131.0 (d)	141.7 (s)	128.6 (d)	128.6 (d)
C-23	40.3 (d)	39.6 (d)	39.6 (d)	41.4 (d)	39.5 (d)	39.5 (d)
C-24	35.4 (t)	40.3 (t)	40.7 (t)	36.9 (t)	32.1 (t)	38.0 (t)
C-25	83.3 (s)	82.9 (s)	82.8 (s)	85.4 (s)	82.8 (s)	82.9 (s)
C-26	201.5 (s)	202.1 (s)	202.0 (s)	201.9 (s)	201.3 (s)	201.3 (s)
C-27	20.2 (q)	18.5 (q)	18.4 (q)	20.6 (q)	18.2 (q)	18.3 (q)
C-28	22.3 (q)	22.3 (q)	22.2 (q)	23.3 (q)	22.3 (q)	22.4 (q)
C-29	13.0 (q)	13.1 (q)	13.1 (q)	13.8 (q)	13.0 (q)	13.2 (q)
C-30	15.2 (q)	15.3 (q)	15.2 (q)	16.0 (q)	15.2 (q)	15.3 (q)
C-31	13.7 (q)	13.1 (q)	14.0 (q)	14.6 (q)	13.1 (q)	14.1 (q)
C-32	64.9 (q)	15.2 (q)	15.2 (q)	65.4 (t)	14.8 (q)	14.9 (q)
C-33	15.0 (q)	28.8 (t)	32.6 (t)	15.5 (q)	28.6 (t)	32.6 (t)
C-34	—	12.7 (q)	21.1 (t)	—	12.6 (q)	21.1 (t)
C-35	—	—	13.01 (q)	—	—	13.1 (q)
C-1E	97.1 (s)	98.0 (d)	98.0 (d)			
C-2E	35.8 (t)	32.3 (t)	38.0 (t)			
C-3E	91.2 (d)	72.7 (s)	72.6 (s)			
C-4E	53.8 (d)	55.5 (d)	55.5 (d)			
C-5E	69.2 (d)	67.7 (d)	67.7 (d)			
C-6E	17.0 (q)	17.2 (q)	17.1 (q)			
3E-CH_3	25.3 (q)	34.2 (q)	32.8 (q)			
4E-$COCH_3$		170.4 (s)	170.5 (s)			
4E-$\underline{C}OCH_3$		23.5 (q)	23.3 (q)			
4E-$\underline{C}OO$	157.4 (s)					
4E-OCH_3	52.6 (q)					

shown in Fig. 2b.

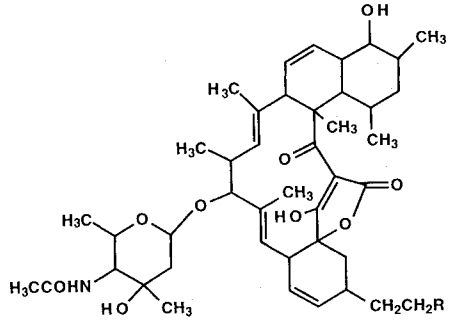
Vigorous methanolysis of saccharocarcin A using 5 M methanolic HCl at room temperature for 20 hours afforded the aglycone **8**. The aglycone was purified by HPLC. The FAB mass spectrum showed *m/z* 551 $(M+H)^+$, 533 $(M+H-H_2O)^+$. The high resolution mass measurements revealed the molecular formula of **8** to be $C_{34}H_{46}O_6$ indicating the absence of nitrogen and presence of twelve degrees of unsaturation in this aglycone. In the ^1H NMR of **8** there are six down field proton signals (δ 6.07, 5.95, 5.46, 5.42, 5.32 and 5.24). The proton signal at δ 6.07 is coupled to proton signal at δ 5.42 and is also connected to proton signal at δ 3.47. These are identified to be protons on C-12, C-11, C-13 respectively. Similarly the other correlation from proton signal at δ 5.95 to 5.46, 3.58 and 2.3 established the relation of C-21, C-22, C-20, C-23 respectively. In the ^{13}C NMR spectrum the low field carbon signals at 206.3 and 202.1 ppm were still present. Comparison of these carbon signals with other tetronic acid derivatives suggested these carbon signals are from C-3 and C-26. The presence of carbon signals at 167.2 and 102.1 ppm are due to C-1 and C-2 respectively, confirmed the tetronic acid moiety. The absence of a carbon signal at 170.4 ppm that was observed saccharocarcin in **1**~**6**, suggested that an ester or amide functional group must be present on one of the sugars. The structure of the aglycone, **8**, was further confirmed by the interpretation of ^1H, ^{13}C NMR, ^1H-^1H COSY, (^{13}C-^1H) long range couplings and HMBC spectral studies.

The ^{13}C NMR of the aglycone **8** and **9**, and the aglycone containing the E sugar (**10** and **11**) of saccharocarcin A and B along with kijanolide (**12**) and kijanosyl kijanolide (**13**) are shown in Table 2. The methyl group at C-16 and the ethyl group at C-23 were established by ^1H-^1H COSY spectra. The aglycone **8** differs from that of kijanimicin by having a methyl and an ethyl groups at C-16 and C-23 respectively and the absence of a hydroxy methyl at C-22.

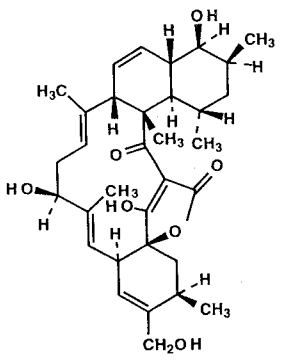
Methanolysis of saccharocarcin A with 0.5 M methanolic HCl at room temperature for 16 hours afforded the compound **10** containing aglycone attached to the E-sugar. The FAB mass spectrum showed the molecular ion peak at *m/z* 736 $(M+H)^+$ revealing the presence of one nitrogen in this molecule. High resolution mass measurements revealed the molecular formula $C_{43}H_{61}NO_9$. It also showed a strong peak at *m/z* 533 indicating a loss of 203 mass units from the parent ion. The high resolution mass measurement of this fragment indicated the molecular formula $C_{34}H_{44}O_5$. It is apparent that the lost fragment ($C_9H_{17}NO_4$) contains nitrogen. The proton signal at δ 4.55 and the carbon signal at 98.0 ppm indicated the presence of one sugar and the IR (1630 cm^{-1}) and ^{13}C NMR (signal at 170.4 ppm) showed the presence of an amide group. The quaternary carbon signal at 72.7 ppm and a singlet methyl signal in ^1H NMR



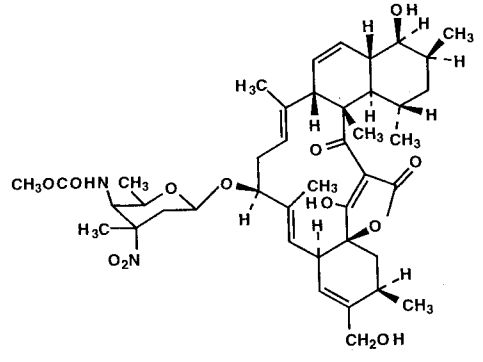
8 R=H
9 R= CH_3



10 R=H
11 R= CH_3



12



13

suggested the C-3 sugar carbon is a quaternary carbon containing the methyl group and an hydroxy group. This structure of the sugar was further strengthened by ^{1}H, ^{13}C and COSY spectral data. Thus in this sugar nitro group of the kijanoside has been substituted by a hydroxyl group and the carbamoyl by an amide.

The sugar sequence was further confirmed by FAB mass spectral fragmentation studies. Saccharocarcin A shows fragment ion peaks at *m/z* 1126, 1110, 996, 866, 736 and 551 in the FAB mass spectrum, which are due to gradual loss of sugars as indicated in Table 3.

Structures of these sugars were confirmed by ^{1}H, ^{13}C and COSY spectra of the parent molecule. Unlike tetrocarcin A, the sugar **C** in these compounds is attached to sugar **B** instead of sugar **D**. This was established by the cleavage of sugars **C** and **D** separately to give fragments with *m/z* 1126 and *m/z* 1110 respectively in the FAB mass spectrum. The stereochemistry of the sugars have not been determined.

Unlike kijanimicin, saccharocarcin A has an additional methyl group on the C-16 but lacks methylene hydroxy on C-22. Kijanimicin also has methyl group instead of ethyl group on C-23. The E-sugar in kijanimicin has a nitro group at C-3 and a carbomoyl group at C-4. However E-sugar in the saccharocarcin family of compounds has a hydroxy group at C-3 and an acetamide group at C-4 position.

Molecular weight, composition and structural components in the other compounds isolated from this fermentation broth are shown in Table 4. The compounds are derived from two homolog aglycones **8** and **9**.

Table 3. FAB mass spectral fragments of saccharocarcin A

1126:	M−C+2H
1110:	M−D+2H
996:	M−C−D+3H
866:	M−C−D−B+2H
736:	M−C−D−B−A+2H
551:	M−C−D−B−A−E+3H
533:	M−C−D−B−A−E+3H−H_2O

Saccharocarcin B (**2**) is 14 mass units higher than **1** and the molecular formula differs by a CH_2 unit indicating it to be a higher homolog of **1**. The fragmentation in FAB mass spectrum did not show the aglycone fragment peak at *m/z* 551 but instead showed a peak at *m/z* 565 which revealed that the aglycone differs by 14 mass units. The position of CH_2 was established based on ^{1}H NMR, ^{13}C NMR and COSY spectral interpretation of the aglycone (**9**). In **2** the ethyl group on C-23 carbon is extended by a methylene to a propyl group.

The molecular formula of saccharocarcin C (**3**) suggested a loss of sugar compared to **1** and **2**, which was confirmed by the presence of only four anomeric protons at δ 5.03, 4.92, 4.89 and 4.55 in ^{1}H NMR and four anomeric carbon signals at 98.5, 91.9, 98.9 and 97.9 ppm in ^{13}C NMR spectrum. However the A-sugar was different from that of **1** and **2** in that it is a 2,3,6-trideoxy sugar. The structure of this sugar was established by ^{1}H NMR, ^{13}C NMR, COSY, SINEPT and HMBC spectral studies.

Saccharocarcin D (**4**) is 16 mass units less than that of **1**. High resolution mass measurements revealed the molecular formula $C_{67}H_{101}NO_{19}$ which is an oxygen less than that of **1**. Further spectral studies revealed that the compound **4** has 2,3,6-trideoxy sugar instead of 2,6 dideoxy sugar as in **1**.

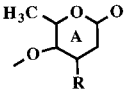
Saccharocarcin E (**5**) is a higher homolog of compound (**3**) and the additional methylene is due to the presence of propyl side chain instead of the ethyl at C-23.

Saccharocarcin F (**6**) is a higher homolog of (**4**) and has a propyl group instead of the ethyl at C-23.

Table 4. Molecular weight, molecular formula and structural features in saccharocarcins **1**~**6**.

Compound	Compound	Molecular weight	Molecular formula	Structural components present
1	Saccharocarcin A	1239	$C_{67}H_{101}NO_{20}$	**8**+A_1+B+C+D+E
2	Saccharocarcin B	1253	$C_{68}H_{103}NO_{20}$	**9**+A_1+B+C+D+E
3	Saccharocarcin C	1109	$C_{61}H_{91}NO_{19}$	**8**+A_2+B+D+E
4	Saccharocarcin D	1223	$C_{67}H_{101}NO_{19}$	**8**+A_2+B+C+D+E
5	Saccharocarcin E	1123	$C_{62}H_{93}NO_{17}$	**9**+A_2+B+D+E
6	Saccharocarcin F	1237	$C_{68}H_{103}NO_{19}$	**9**+A_2+B+C+D+E

A_1 R=−OH
A_2 R=−H



Experimental

General Procedures

Solvents employed for chromatography were obtained from Fisher Scientific, Fair Lawn, NJ, 07410. Semi-preparative reverse phase HPLC was carried out on a μBondapak C-18 silica column obtained from Waters Corporation, Milford, MA.

The melting points are uncorrected. IR spectra were determined on a Nicolet FTIR model 10-MX instrument. Ultraviolet spectra were obtained by using a Hewlett Packard '8450 A' UV-vis spectro-photometer equipped with HP-9872B plotter. All FAB mass spectra were obtained on a Finnigan MAT-312 mass spectrometer. Cs^+ ion liquid secondary ion mass spectra (SIMS) and high resolution mass measurements were obtained on a VG-ZAB-SE mass spectrometer using a glycerol-thioglycerol or *m*-nitrobenzyl alcohol matrix with the sample dissolved in dimethyl sulfoxide. NMR spectra were measured on a Varian XL-300 instrument operating at 300 and 75 MHz for ^1H and ^{13}C respectively. ^1H and ^{13}C NMR spectra were recorded relative to TMS as an internal standard. 2D NMR spectra were measured on a Varian XL-400 and GE-400 NMR instruments.

Methanolysis of **1** to Isolate **10**

1 (0.5 g) was dissolved in 0.5 M methanolic hydrogen chloride (500 ml) and the solution was stirred at 25°C under nitrogen for 20 hours. Concentrated ammonium hydroxide (30 ml) was added and the mixture was evaporated to dryness under reduced pressure. The residue was extracted with methylene chloride, filtered and washed with excess methylene chloride and the filtrate was dried. The residue was purified on a Water's reverse phase semi-preparative column eluting with a mixture (6 : 4) of methanol and 0.01 M sodium dihydrogen phosphate (pH 6.5). The eluate containing **10** was collected, the methanol removed and extracted with methylene chloride. The methylene chloride layer is separated, dried over sodium sulfate and solvent removed to yield 207 mg of **10**.

Methanolysis of **1** to Isolate **8**

1 (0.5 g) was dissolved in 5 M hydrogen chloride in methanol (350 ml) and the solution was stirred at 25°C under nitrogen for 20 hours. Concentrated ammonium hydroxide (195 ml) was added and the solution was evaporated to dryness under reduced pressure. The residue was extracted with methylene chloride, filtered and washed with excess methylene chloride. The organic extract was dried over anhydrous sodium sulfate and the solvent removed. The extract was purified on a Water's semi-preparative reverse phase column eluting with a mixture (6 : 4) of methanol and 0.01 M sodium dihydrogen phosphate (pH 6.5). The eluate containing **8** was collected, the methanol removed and then extracted with methylene chloride. The methylene chloride layer was separated, dried over sodium sulfate and solvent removed to yield 186 mg of **8**.

Methanolysis of **2** to Isolate **11**

2 (0.5 g) was subjected to mild methanolysis using 0.5 M hydrogen chloride in methanol, using the above procedure to obtain 211 mg of **11**.

Methanolysis of **2** to Isolate **9**

2 (0.5 g) was subjected to vigorous methanolysis using 5 M hydrogen chloride in methanol, using the above procedure to obtain 195 mg of **9**.

Saccharocarcin A (**1**): mp 220°C; $[\alpha]_D^{23} = -172.8°$ (MeOH, 0.0013); UV (MeOH) λ_{max}, nm: 205 (13700), 240 (13050), 267 (12115), (MeOH + HCl): 207 (38900), 262 (10375), (MeOH + NaOH): 211 (53030), 266 (12800), 366 (990); IR (KBr) ν_{max}: 3440, 2975, 2930, 1755, 1630, 1555 1420, 1385, 1060, 975 cm^{-1}; FAB-MS: *m/z* 1240 $(M+H)^+$, 1126, 978, 866, 736, 533; HRFAB-MS: Measured 1262. 6877 $(M+Na)^+$, calcd. for $C_{67}H_{101}NO_{20}Na$ 1262.6815; ^1H NMR ($CDCl_3$): δ 5.92 (dt, $J=10$, 0.5 Hz, 1H), 5.83 (d, $J=10$ Hz, 1H), 5.74 (d, $J=1$ Hz, 1H), 5.4 (dt $J=10$, 1 Hz, 1H), 5.37 (m, 1H), 5.23 (d, $J=10$ Hz, 1H), 5.18 (d, $J=11$ Hz, 1H), 5.15 (d, $J=5$ Hz, 1H), 4.96 (dd, $J=10$, 2 Hz,1H), 4.94 (s, 1H), 4.82 (d, $J=5$ Hz, 1H), 4.57 (dd, $J=10$, 2 Hz, 1H), 4.26 (m, 2H), 4.12 (q, $J=7$ Hz, 1H), 4.02 (m, 3H), 3.9 (m, 2H), 3.74 (d, $J=10$ Hz, 1H), 3.75 ~ 3.6 (m, 3H), 3.55 (d, $J=10$ Hz, 1H), 3.47 (dd, $J=$ 11, 5 Hz, 1H), 3.4 (dd, $J=10$, 3 Hz, 1H), 3.35 (d, $J=4$ Hz, 1H), 3.32 (dd, $J=10$, 4 Hz, 1H), 3.2 ~ 3.4 (d, 2H), 2.36 (dd, $J=9$, 3 Hz, 1H), 2.26 (s, 1H), 2.45 (t, $J=8$ Hz, 1H), 2.37 (dd, $J=16$, 2 Hz, 1H), 2.2 ~ 2.35 (m, 4H), 2.16 (dd, $J=16$, 2Hz, 1H), 2.08 (s, 3H), 2.05 (m, 1H), 1.7 ~ 2.0 (several protons), 1.84 (s, 3H), 1.64 (s, 3H), 1.64 ~ 1.44 (m, 5H), 1.44 (s, 3H), 1.36 (s, 3H), 1.32 (d, $J=6$ Hz, 3H), 1.28 (d, $J=6$ Hz, 3H), 1.26 (d, $J=6$ Hz, 3H), 1.24 (s, 3H), 1.20 (d, $J=6$ Hz, 3H), 1.12 (d, $J=7$ Hz, 3H), 1.07 (d, $J=7$ Hz, 3H), 1.0 (d, $J=7$ Hz, 3H), 0.96 (t, $J=7$ Hz, 3H), 0.64 (d, $J=5$ Hz, 3H).

Saccharocarcin B (**2**): mp 210°C; $[\alpha]_D^{23} = -162.2°$ (MeOH, 0.0012); UV (MeOH) λ_{max} : 205, 240, 267 nm; IR (KBr) ν_{max}: 3430, 2975, 2925, 1765, 1730, 1555, 1455, 1385, 1125, 1060, 990 cm^{-1}; FAB-MS: *m/z* 1254 $(M+H)^+$, 1140, 1011, 993, 880, 750, 547; HRFAB-MS: Measured $(M+Na)^+$ 1276.7004, calcd. for $C_{68}H_{103}NO_{20}Na$ 1276.6971; ^1H NMR ($CDCl_3$): δ 5.9 (dt, $J=11$, 0.5 Hz, 1H), 5.8 (d, $J=10$ Hz, 1H), 5.72 (d, $J=10$ Hz, 1H), 5.4 (m, 2H), 5.1 ~ 5.3 (m, 3H), 4.96 (dd, $J=10$, 2 Hz, 1H), 4.92 (s, 1H), 4.82 (d, $J=5$ Hz, 1H), 4.55 (dd, $J=10$, 2 Hz, 1H), 4.25 (m, 2H), 4.15 (dq, $J=7$, 0.5 Hz, 1H), 4.0 (m, 3H), 3.9 (m, 2H), 3.2 ~ 3.7 (m, 11H), 3.58 (d, $J=10$ Hz, 1H), 3.4 (dt, $J=11$, 0.5 Hz, 1H), 3.37 (m, 1H), 3.3 (m, 1H), 3.15 (m, 4H), 2.4 (dt, $J=9$, 2 Hz, 1H), 2.3 ~ 2.05 (several protons), 1.97 (s, 3H), 1.7 (d, $J=14$ Hz, 2H), 2.05 ~ 1.4 (several protons), 1.5 (s, 3H), 1.3 (s, 3H), 1.25 (s, 3H), 1.25 (d, $J=7$ Hz, 3H), 1.2 (s, 3H), 1.0 (s, $J=7$ Hz, 3H), 1.0 (m, 2H), 0.9 (d, $J=7$ Hz, 3H), 0.82 (t, $J=7$ Hz, 3H), 1.04 ~ 1.08 (several protons), 0.65 (d, $J=5$ Hz, 3H).

Saccharocarcin C (**3**): mp 202°C; $[\alpha]_D^{24} = -150.6°$ (MeOH, 0.0015); UV (MeOH) λ_{max}: 205, 240, 267 nm; IR (KBr) ν_{max}: 3435, 2980, 2930, 1765, 1665, 1635, 1455, 1385, 1125, 1070, 985 cm^{-1}; FAB-MS: *m/z* 1110 $(M+H)^+$, 980, 850, 736, 533; HRFAB-MS: Measured $(M+H)^+$ 1110.6356, calcd for $C_{61}H_{92}NO_{17}$ 1110.6365; ^1H NMR ($CDCl_3$): δ 5.9 (dt, $J=10$, 3 Hz, 1H), 5.86 (d, $J=11$ Hz, 1H), 5.74 (d, $J=11$ Hz, 1H), 5.37 (dt, $J=10$, 1 Hz,1H), 5.35 (m, 1H), 5.2 (d, $J=9$ Hz, 1H), 5.14 (dd, $J=11$, 0.5 Hz, 1H), 5.03 (d, $J=4$ Hz, 1H), 4.92 (dd, $J=10$, 2 Hz, 1H), 4.89 (s, 1H), 4.55 (dd, $J=8$, 2 Hz, 1H), 4.07 (dd, $J=6$, 4 Hz, 1H), 3.89 (s, 1H), 3.83 (dd, $J=9$, 10 Hz, 1H), 3.74 (dd, $J=6$, 1.5 Hz, 1H), 3.65 (d, $J=10$ Hz, 1H), 3.25 (dd, $J=10$, 3 Hz, 1H), 2.56 (b, 1H), 2.46 (dt, $J=2$, 9 Hz, 1H), 2.34 (b, 1H), 2.3 (t, $J=7$ Hz, 1H), 2.22 (b, 2H), 2.06 ~ 2.18 (m, 2H), 2.2 (s, 3H), 2.02 ~ 1.92 (m, 4H), 1.86 ~ 1.62 (several protons), 1.6 (s, 3H), 1.62 ~ 1.42 (m, 2H), 1.4 (s, 3H), 1.34 (s, 3H), 1.28 (d, $J=6$ Hz, 3H), 1.26 (d, $J=6$ Hz, 3H), 1.24 (s, 3H), 1.23 (d, $J=6$ Hz, 3H), 1.09 (d, $J=7.5$ Hz, 3H), 1.06 (d, $J=7$ Hz, 3H), 0.97 (d, $J=7$ Hz, 3H), 0.96 (t, $J=7$ Hz, 3H), 0.64 (d, $J=5$ Hz, 3H).

Saccharocarcin D (**4**): mp 208°C; $[\alpha]_D^{23} = -149.6°$ (MeOH, 0.0011); UV (MeOH) λ_{max}: 205, 240, 267 nm; IR (KBr) ν_{max}: 3440, 2975, 2930, 1755, 1665, 1630, 1455, 1375, 1125, 1055, 975 cm^{-1}; FAB-MS: *m/z* 1224 $(M+H)^+$, 1111, 959, 850, 736, 533; HRFAB-MS: Measured $(M+Na)^+$ 1246.6859, calcd for $C_{67}H_{101}NO_{19}Na$ 1246.6865; ^1H NMR ($CDCl_3$): δ 5.9 (dt, $J=10$, 2 Hz, 1H), 5.8 (d, $J=10$ Hz, 1H), 5.75 (d, $J=10$ Hz, 1H), 5.38 (m, 2H), 5.22 (d, $J=9$ Hz, 1H), 5.16 (d, $J=11$ Hz, 1H), 5.08 (d, $J=11$ Hz, 1H), 5.03 (d, $J=4$ Hz, 1H), 4.95 (dd, $J=10$, 2 Hz, 1H), 4.92 (d, $J=4$ Hz, 1H), 4.8 (d, $J=1$ Hz, 1H), 4.55 (dd, $J=10$, 2 Hz, 1H), 4.27 (dd, $J=6$, 1 Hz, 1H), 4.1 (m, 2H), 3.89 (s, 1H), 3.85 (m, 2H), 3.67 (d, $J=10$ Hz, 1H), 3.63 (m, 2H), 3.53 (dd, $J=11$, 5 Hz, 2H), 3.45 (dd, $J=10$, 3 Hz, 1H), 3.37 (d, $J=5$ Hz, 2H), 3.31 (m, 1H), 3.23 (dd, $J=10$, 3 Hz, 2H), 2.47 (dt, $J=7$, 2 Hz, 1H), 2.34 ~ 2.1 (m, 6H), 2.05 (s, 3H), 2.1 ~ 2.2 (m, 2H), 2.0 (m, 3H), 1.93 ~ 1.64 (several protons), 1.6 (s, 3H), 1.64 ~ 1.4 (m, 5H), 1.41 (s, 3H), 1.36 (s, 3H), 1.31 (d, $J=6$ Hz, 3H), 1.07 (d, $J=5$ Hz, 3H), 0.99 (d, $J=6$ Hz, 3H), 0.97 (t, $J=7$ Hz, 3H), 0.65 (d, $J=4$ Hz, 3H).

Saccharocarcin E (**5**): mp 187°C; $[\alpha]_D^{23} = -131.8°$ (MeOH, 0.0008); UV (MeOH) λ_{max}: 205, 240, 267 nm; IR (KBr) ν_{max}: 3430, 2965, 2930, 1750, 1630, 1455, 1440, 1385, 1125, 1070, 985 cm^{-1}; FAB-MS: *m/z* 1124 $(M+H)^+$, 995, 864, 750, 547; Molecular formula: $C_{62}H_{93}NO_{17}$; ^1H NMR ($CDCl_3$): δ 5.87 (dt, $J=10$ Hz, 1H), 5.77 (d, $J=10$ Hz, 1H), 5.74 (d, $J=10$ Hz, 1H), 5.37 (m, 2H), 5.22 (d, $J=9$ Hz, 1H), 5.16 (d, $J=11$ Hz, 1H), 5.03 (d, $J=4$ Hz, 1H), 4.93 (dd, $J=10$, 2 Hz, 1H), 4.8 (d, $J=0.5$ Hz, 1H), 4.55 (dd, $J=10$, 2 Hz, 1H), 4.2 (m, 1H), 4.1 (m, 3H), 3.89 (s, 1H), 3.84 (dt, $J=9$, 3 Hz, 1H), 3.75 (dt, $J=10$, 3 Hz, 1H), 3.65 (m, 3H), 3.54 (m, 2H), 3.36 (m, 3H), 3.26 (s, 1H), 3.25 (dd, $J=7$, 3 Hz, 1H), 2.47 (dt, $J=9$, 2Hz, 1H), 2.4 ~ 2.25 (m, 3H), 2.25 ~ 2.1 (m, 4H), 2.05 (s, 3H), 2.1 ~ 1.75 (m, several protons), 1.6 (s, 3H), 1.75 ~ 1.46 (several protons), 1.41 (s, 3H), 1.35 (s, 3H), 1.46 ~ 1.38 (m, 2H), 1.38 ~ 1.33 (m, 1H), 1.29 (d, $J=7$Hz, 3H), 1.27 (d, $J=7$ Hz, 3H), 1.25 (s, 3H), 1.24 (d, $J=7$ Hz, 3H), 1.14 (m, 2H), 1.1 (d, $J=9$ Hz, 1H), 1.07 (d, $J=7$ Hz, 3H), 0.98 (d, $J=7$ Hz, 3H), 0.92 (t, $J=7$ Hz, 3H), 0.65 (d, $J=4$ Hz, 3H).

Saccharocarcin F (**6**): mp 192°C; UV (MeOH) λ_{max}: 205, 240, 267 nm; IR (KBr) ν_{max}: 3435, 2965, 2930, 1715, 1630, 1455, 1410, 1385, 1125, 1055, 990 cm^{-1}; FAB-MS: *m/z* 1238 $(M+H)^+$, 1124, 864, 750, 679, 619, 547; Molecular formula: $C_{68}H_{103}NO_{19}$; ^1H NMR ($CDCl_3$): δ 5.87 (dt, $J=11$, 2 Hz, 1H), 5.83 (d, $J=10$ Hz, 1H), 5.75 (d, $J=10$ Hz, 1H), 5.37 (m, 2H), 5.22 (d, $J=9$ Hz, 1H), 5.16 (d, $J=10.5$ Hz, 1H), 5.03 (d, $J=4$ Hz, 1H), 4.95 (dd, $J=10$, 2 Hz, 1H), 4.92 (s, 1H), 4.79 (s, 1H), 4.55 (dd, $J=10$, 2 Hz, 1H), 4.26 (dd, $J=10$, 2 Hz, 1H), 4.2 (dt, $J=3$, 3 Hz, 1H), 4.08 (dt, $J=7$, 9 Hz, 1H), 3.9 (s, 1H), 3.85 (m, 2H), 3.65 (m, 5H), 3.54 (dd, $J=11$, 5 Hz, 1H), 3.45 (dd, $J=10$, 3 Hz, 1H), 3.38 (m, 1H), 3.26 (dd, $J=7$, 3 Hz, 1H), 3.24 (s, 1H), 2.45 (dt, $J=10$, 2 Hz, 1H), 2.4 ~ 2.25 (m, 2H), 2.2 (m, 3H), 2.05 (s, 3H), 1.95 (m, 2H), 1.9 ~ 1.5 (several protons), 1.5 (s, 3H), 1.41 (s, 3H), 1.5 ~ 1.37 (m, 2H), 1.35 (s, 3H), 1.3 (d, $J=7$ Hz, 3H), 1.27 (d, $J=7$ Hz, 3H), 1.25 (s, 3H), 1.23 (d, $J=5$ Hz, 3H), 1.14 (d, $J=7$ Hz, 3H), 1.1 (d, $J=7$ Hz, 3H), 1.07 (d, $J=7$ Hz, 3H), 0.98 (d, $J=7$ Hz, 3H), 0.92 (t, $J=7$ Hz, 3H), 0.64 (d, $J=5$ Hz, 3H).

Aglycone of saccharocarcin A (**8**): UV (MeOH) λ_{max}: 215, 247, 263 nm; IR (KBr) ν_{max}: 3459, 2956, 2924, 1751, 1738, 1635, 1448, 1377, 984 cm^{-1}; FAB-MS: 551 $(M+H)^+$; HR-MS: Measured 533.3267 $(M+H-H_2O)^+$, calcd 533.3285 for $C_{34}H_{45}O_5$ $(M+H-H_2O)^+$; ^1H NMR ($CDCl_3$): δ 6.07 (dt, $J=10$, 1 Hz, 1H), 5.95 (dt, $J=10$, 2 Hz, 1H), 5.46 ~ 5.42 (m, 2H), 5.32 (dt, $J=10$, 0.5 Hz, 1H), 5.24 (d, $J=10$ Hz, 1H), 3.9 (s, 1H), 3.68 (dd, $J=10$, 5 Hz, 1H), 3.58 (ddd, $J=11$, 4, 2 Hz, 1H), 3.47 (d, $J=5$ Hz, 1H), 2.55 (m, 1H), 2.3 (m, 3H), 2.05 (m, 2H), 1.86 (d, $J=16$ Hz, 1H), 1.7 (m, 1H), 1.6 (several protons), 1.43 (s, 3H), 1.40 (s, 3H), 1.04 (d, $J=7$ Hz, 3H), 1.00 (d, $J=7$ Hz, 3H), 0.98 (t, $J=7$ Hz, 3H), 0.65 (d, $J=5$ Hz, 3H).

Aglycone of saccharocarcin B (**9**): UV (MeOH) λ_{max}: 215, 249, 265 nm. IR (KBr) ν_{max}: 3459, 2962, 2937, 1764, 1750, 1622, 1583, 1454, 1377, 984 cm^{-1}; FAB-MS: *m/z* 565 $(M+H)^+$, 547; Molecular formula: $C_{35}H_{48}O_6$; ^1H NMR ($CDCl_3$): δ 6.03 (d, $J=10$ Hz, 1H), 5.9 (dt, $J=10$, 1 Hz, 1H), 5.43 (m, 2H), 5.28 (d, $J=10.5$ Hz, 1H), 5.22 (d, $J=10$ Hz, 1H), 3.88 (s, 1H), 3.66 (dd, $J=10$, 5 Hz, 1H), 3.55 (dq, $J=10.5$, 2 Hz, 1H), 3.45 (d, $J=5$ Hz, 1H), 2.53 (dt, $J=4$, 1 Hz, 1H), 2.31 (m, 3H), 2.05 (m, 2H), 1.82 (d, $J=15$ Hz, 1H), 1.8 ~ 1.46 (several protons), 1.61 (s, 3H), 1.42 (s, 3H),1.4 (m, 1H), 1.39 (s, 3H), 1.26 (m, 1H), 1.04 (d, $J=7$ Hz, 3H), 1.01 (d, $J=7$ Hz, 3H), 0.92 (t, $J=7$ Hz, 3H), 0.65 (d, $J=5$ Hz, 3H).

Aglycone with E-sugar of saccharocarcin A (**10**): UV (MeOH) λ_{max}: 215, 242, 265 nm; IR (KBr) ν_{max}: 3433, 2962, 2930, 1764, 1673, 1628, 1454, 1370, 1061 cm^{-1}; FAB-MS: 736 $(M+H)^+$; HR-MS: Measured 736.4408

$(M+H)^+$, calcd 736.4426 for $C_{43}H_{62}NO_9$ $(M+H)^+$; ^1H NMR ($CDCl_3$): δ 6.02 (d, $J=10$ Hz, 1H), 5.92 (dt, $J=10$, 1 Hz, 1H), 5.8 (d, $J=10$ Hz, 1H), 5.4 (m, 2H), 5.23 (d, $J=9$ Hz, 1H), 5.17 (d, $J=10.5$ Hz, 1H), 4.55 (dd, $J=10$, 2 Hz, 1H), 4.1 (dt, $J=6$, 1 Hz, 1H), 3.89 (s, 1H), 3.68 (d, $J=10$ Hz, 1H), 3.64 (m, 2H), 3.54 (dq, $J=11$, 2 Hz, 1H), 3.39 (d, $J=5$ Hz, 1H), 2.48 (m, 1H), 2.28 (m, 3H), 2.06 (s, 3H), 1.82 (t, $J=4$ Hz, 2H), 1.72 (dt, $J=8$, 7 Hz, 1H), 1.63 (s, 3H), 1.58~1.4 (several protons), 1.44 (m, 1H), 1.4 (s, 3H), 1.37 (s, 3H), 1.25 (s, 3H), 1.06 (d, $J=6$ Hz, 3H), 1.04 (d, $J=8$ Hz, 3H), 0.98 (d, $J=7$ Hz, 3H), 0.96 (t, $J=7$ Hz, 3H), 0.66 (d, $J=5$ Hz, 3H).

Aglycone with E-sugar of saccharocarcin B (**11**): UV (MeOH) λ_{max}: 215, 243, 264 nm; IR (KBr) ν_{max}: 3433, 2962, 2924, 1757, 1660, 1454, 1383, 1061, 984 cm^{-1}; FAB-MS: m/z 750 $(M+H)^+$; Molecular formula: $C_{44}H_{63}NO_9$; ^1H NMR ($CDCl_3$): δ 6.03 (d, $J=10$ Hz, 1H), 5.89 (dt, $J=10$, 1 Hz, 1H), 5.82 (d, $J=10$ Hz, 1H), 5.4 (m, 2H), 5.23 (d, $J=10.5$ Hz, 1H), 5.18 (d, $J=10.5$ Hz, 1H), 4.56 (dd, $J=10$, 2 Hz, 1H), 4.10 (dt, $J=6$, 1 Hz, 1H), 3.9 (s, 1H), 3.68 (d, $J=10$ Hz, 1H), 3.65 (m, 1H), 3.53 (dq, $J=11$, 2 Hz, 1H), 3.38 (d, $J=5$ Hz, 1H), 2.48 (m, 1H), 2.3 (m, 3H), 2.06 (s, 3H), 1.9~1.7 (m, 4H), 1.62 (s, 3H), 1.7~1.3 (several protons), 1.42 (s, 3H), 1.39 (s, 3H), 1.25 (s, 3H), 1.08 (d, $J=7$ Hz, 3H), 1.03 (d, $J=7$ Hz, 3H), 1.00 (d, $J=7$ Hz, 3H), 0.92 (t, $J=7$ Hz, 3H), 0.65 (d, $J=5$ Hz, 3H).

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