12.7 Å, in which the CsCl and mixed KCl/CsCl salt reside, respectively. The salt can be removed by washing at room temperature to give the microporous compound $Cs_2Cu_3(P_2O_7)_2 \cdot 8.5\,H_2O$.

[9] Using a stoichiometric mixture of $Na_2O/2\,CsCl/3\,CuO/2\,P_2O_5$, reactions by both slow cooling and quenching were studied after heating at 550 °C for a day. The quenched reaction gave a high-yield product (ca. 80 %) of CU-4, while the slow-cooled reaction gave a mixture of the CU-4 phase (ca. 50 %) and unknown products. The thermogravimetric analysis results show that the CU-4 phase decomposes at ~560 °C, and further studies suggest that the temperature window in which the CU-4 phase exists is ca. 500 – 550 °C.

[10] Crystal data of $Na_2Cu_3(P_2O_7)_2 \cdot 2\,CsCl$: colorless column crystal ($0.53 \times 0.18 \times 0.14$ mm^3), $M_r = 921.2$, tetragonal $P4_2/mnm$ (no. 136), $a = b = 15.868(2)$, $c = 13.238(2)$ Å, $V = 3333.1(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 3.671$ g cm^{-3}, $\mu = 89.24$ cm^{-1}. Data collection: Nicolet R3mV diffractometer, ω-2θ scan mode, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation, $T = 295$ K. A total of 2119 unique reflections measured, of which 1715 ($F > 4.0\sigma(F)$) were used for the structure solution. Lorentz, polarization and empirical absorption corrections based on three azimuthal scans ($2\theta = 18.19°$, 22.01°, 24.72°) were applied to the intensity data (transmission factors: 0.43 – 0.62). The SHELXTL-Plus software package was used for crystal structure solution and refinement. The structure was solved by direct methods using the SHELXS-86 program and refined on $|F|$ by least-squares, full-matrix techniques. Final $R/R_W = 0.032/0.040$, GOF = 1.14 for 145 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of -1.49 and $+1.88$ e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411491. TEXSAN: Single Crystal Structure Analysis Software, Version 1.6b, Molecular Structure Corp., The Woodlands, TX, **1993**; "Scattering Factors for Non-Hydrogen Atoms": D. T. Cromer, J. T. Waber, *International Tables for X-ray Crystallography*, *Vol. IV*, Kynoch Press, Birmingham, **1974**, Table 2.2 A, pp. 71 – 98; G. M. Sheldrick in *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard), Oxford University Press, London, **1985**, pp. 175 – 189; G. M. Sheldrick, SHELXS-93, Göttingen, Germany, **1993**.

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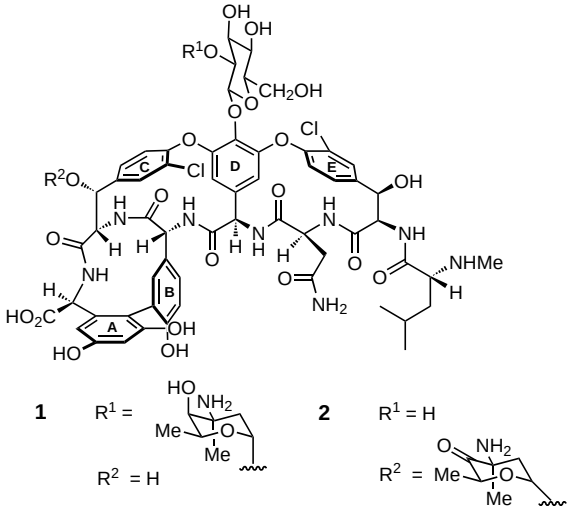
The Biosynthesis of Vancomycin-Type Glycopeptide Antibiotics—New Insights into the Cyclization Steps**

Daniel Bischoff, Stefan Pelzer, Alexandra Höltzel, Graeme J. Nicholson, Sigrid Stockert, Wolfgang Wohlleben, Günther Jung, and Roderich D. Süssmuth*

Over recent years, vancomyin (**1**) (Scheme 1)[1] has emerged as an antibiotic of last resort against infections of methicillin-resistant *Staphylococcus aureus* (MRSA) strains.[2] The antibiotic activity of the vancomycin-related glycopeptides is based on the high specificity of the aglycon cavity



Scheme 1. Structures of the glycopeptide antibiotics vancomycin (**1**) and balhimycin (**2**).

towards the *N*-acyl-D-Ala-D-Ala-peptide motif of bacterial cell-wall precursors.[3] Besides its pharmaceutical significance, work on the total synthesis of vancomycin has attracted the attention of synthetic chemists on account of the highly challenging stereochemical requirements encountered in the synthesis of the tricyclic aglycon. Chemical and biological aspects of glycopeptide antibiotics have been extensively reviewed recently.[4]

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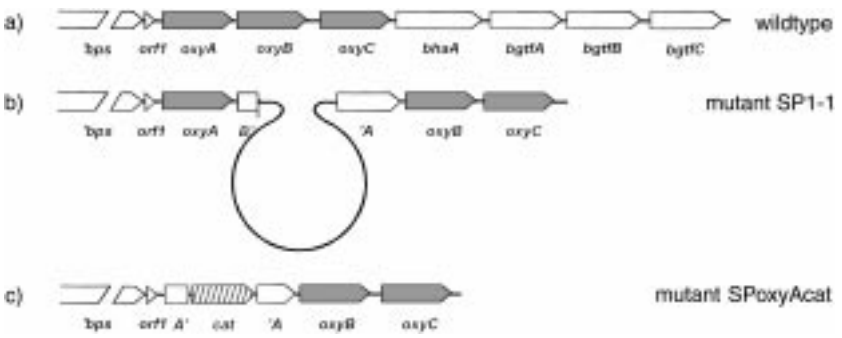


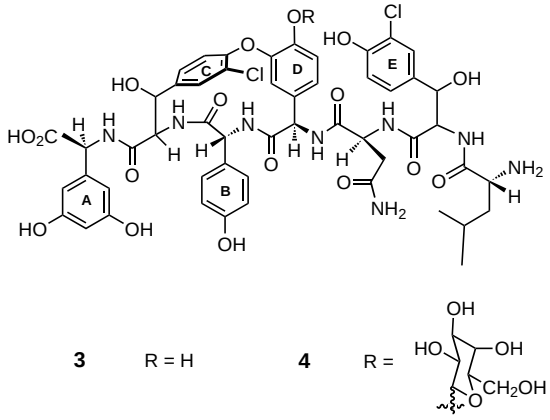
Figure 1. a) Gene organization of a part of the balhimycin biosynthetic gene cluster from *A. mediterranei* wildtype. b) The gene inactivation mutant SP1-1 after integration of plasmid pSP1.5Pst.[8] c) The *oxyA* gene replacement mutant SPoxyAcat. (*'bps* = part of a peptide synthetase gene; *orfI* = Orf with unknown function; *oxyA* – *C* = oxygenase genes; *bhaA*: halogenase gene; *bgtfA* – *C*: glycosyltransferase genes; *A'*/*'A* = parts of the *oxyA* gene; *B'* = part of the *oxyB* gene; *cat* = chloramphenicol resistance gene)

The aim of our investigations was to reveal the order of the oxidative bridging in the aromatic side chains during the biosynthetic formation of the aglycon unit. Sequence homology studies indicated[5] that the aglycon ring system, which includes one biaryl bond and two diaryl ether bridges, is possibly formed from a linear precursor peptide by the action of three oxygenases (*oxyA*/*B*/*C*). This was previously confirmed for balhimycin (**2**), a glycopeptide antibiotic of the vancomycin type produced by *Amycolatopsis mediterranei DSM 5908* (Scheme 1).[6] The inactivation of oxygenase genes resulted in a mutant (SP1-1; Figure 1), from which the two peptides SP-1134 and SP-969 were isolated and suggested to be linear precursor peptides of the aglycon.[7, 8] However, the sequence of the oxidation steps still remains elusive. Therefore we have continued our studies of the oxygenase genes by constructing an *oxyA* gene replacement mutant bearing a chloramphenicol resistance gene (*cat*) (Figure 1). The correct gene replacement event was proven by means of Southern hybridization. From this mutant we were able to isolate for the first time peptides with only one diaryl ether bridge (Scheme 2).

The culture filtrate of this mutant (SPoxyAcat) showed no antibiotic activity. From the supernatant, two compounds (SP-1132 **3** and SP-1294 **4**) were isolated by adsorption chromatography and preparative RP-HPLC. Structural characterization was achieved by means of ES-quadrupole MS and tandem MS experiments, ES-FTICR-MS, Edman degradation, 2D NMR spectroscopy, and amino acid and sugar analysis by GC-MS.

Molecular masses of 1132.2984 Da (**3**) and 1294.3512 Da (**4**) were determined by FTICR-MS. Both compounds showed the characteristic isotopic pattern for two chlorine atoms (Figure 2a). Chiral amino acid analysis revealed that L-Asn, D-Leu, D-4-hydroxyphenylglycine (Hpg), and L-3,5-dihydroxyphenylglycine (Dpg) are constituents of **3** and **4**. The primary peptide sequence ^{1}Leu-^{2}Cht-^{3}Asn-^{4}—^{5}Hpg-^{6}—^{7}Dpg was determined by Edman degradation for both compounds. No amino acid was detected in cycles 4 and 6, which suggests that ^{4}Hpg and ^{6}Cht are connected by a diaryl ether bridge. The sugar analysis of **4** by GC-MS revealed the presence of galactose (Gal).

ES-MS/MS experiments (Figure 2b) and 2D NMR experiments (Tables 1 and 2) confirmed these results, and we were able to elucidate the structure of SP-1132 (**3**; Scheme 2). ^{1}H and ^{13}C NMR chemical shifts were assigned by means of TOCSY, P.E. (primitive exclusive) COSY, NOESY, HSQC,



Scheme 2. Structures of SP-1132 (**3**) and SP-1294 (**4**).

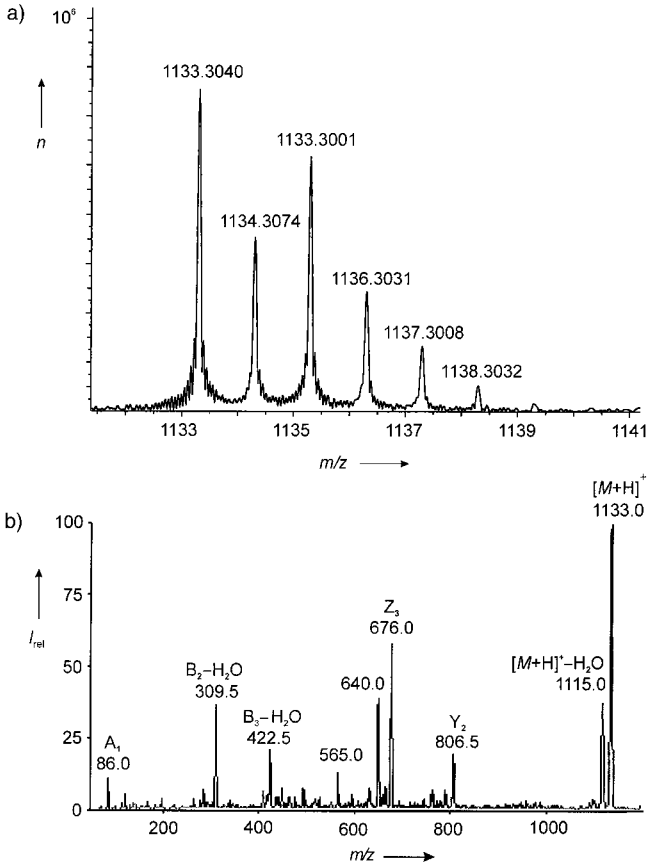


Figure 2. Mass spectrometric data of SP-1132 (**3**). a) High-resolution ES-FTICR mass spectrum with the characteristic isotope distribution pattern. b) ES-MS/MS daughter-ion spectrum with the assignments of fragments.

  1433-7851/01/4009-1694 $ 17.50+.50/0

Table 1. ^{1}H and ^{13}C NMR shifts of peptide SP-1132 (**3**) ([D$_6$]DMSO, 305 K).

	N/C′ δ [ppm]	α δ [ppm]	β δ [ppm]	Others δ [ppm]
[1]Leu		3.60	1.36	γ: 1.45, δ: 0.77/0.76
	168.7	51.0	39.7	γ: 23.3, δ: 21.4/22.7
[2]Cht	8.51	4.49	4.66	OH$^{\gamma}$: 5.58, 2: 7.31, OH^4: 10.02
	169.4	58.5	71.9	1: 133.7, 2: 128.4, 4: 152.2, 3: 119.1
				5: 6.84, 6: 7.07
				5:115.9, 6:126.8
[3]Asn	8.32	4.71	2.57/2.45	δ: 7.35/6.90
	170.1	49.7	37.4	γ: 171.6
[4]Hpg	7.91	5.48	–	2: 6.57, OH^4: 9.42
	168.1	54.1	–	2: 114.2, 4: 145.6, 1: 128.3, 3: 146.3
				5: 6.84, 6: 6.72
				5: 116.3, 6: 120.5
[5]Hpg	8.51	5.22	–	2,6: 7.22, 3,5: 6.78, OH^4: 9.57
	168.1	56.6	–	2,6: 129.6, 3,5: 115.4, 4: 157.3, 1: 126.3
[6]Cht	6.48	4.59	5.32	OH$^{\gamma}$: 5.55, 2: 7.68
	167.6	58.6	71.8	1: 140.1, 2: 128.8, 3: 125.2, 4: 149.9,
				5: 7.20, 6: 7.39
				5: 123.4, 6: 125.0
[7]Hpg	8.86	5.13	–	2,6: 6.25, OH^{3,5}: 9.34, 4: 6.15
	171.7	56.3	–	2,6: 105.4, 3,5: 158.4, 4: 102.1, 1: 139.2

and HMBC spectroscopic analysis. The sequence of the aglycon was reflected in numerous interresidue cross-peaks observed in the NOESY ($H^N_{i+1} \leftrightarrow H^{\alpha}_i$) and the HMBC ($H^N_{i+1} \leftrightarrow C'_i$) spectra. The position of the sugar moiety of **4** was determined by NOE interactions between H1′-Gal and both H5- and H6-^{4}Hpg as well as by an HMBC connectivity between H1′-Gal and C4-^{4}Hpg. The molecular formulae of $C_{52}H_{54}Cl_2N_8O_{17}$ (**3**) and $C_{58}H_{64}Cl_2N_8O_{22}$ (**4**) deduced from the NMR experiments are in agreement with the molecular formulae determined by high-accuracy FTICR-MS measurements for **3** (relative error: 1.5 ppm) and **4** (relative error: 3.0 ppm).

Compounds SP-1132 (**3**) and SP-1294 (**4**) are the first examples of singly bridged peptides that were isolated from a glycopeptide antibiotic producing organism. No linear peptides such as SP-1134 or SP-969 were detected in the culture filtrate of the mutant SPoxyAcat. The stereochemistry of the amino acids, and the chlorination and β-hydroxylation patterns of **3** and **4** are identical to those of the linear peptide SP-1134. Of the two possible atropisomers of the C-*O*-D ring, only the naturally occurring one has been observed.[9] This means that the oxygenase (either intact oxyB or oxyC) specifically recognizes and quantitatively converts the linear precursor peptide into the naturally occurring atropisomer. Galactose is bonded to ^{4}Hpg in **4** as the result of an unspecific glycosylation, as galactosylation has so far not been observed in balhimycin derivatives. The results herein support the hypothesis that β-hydroxylation and chlorination occur before the oxidative ring formation of the aglycon, and that glycosylation and N-methylation occur subsequently.[7,8,10,11] We consider that the formation of the C-*O*-D ring system is the first ring-closure reaction in the oxidative bridging of the aglycon biosynthesis, and this is the subject of our current investigations.

Experimental Section

The SPoxyAcat-Mutant of *Amycolatopsis mediterranei DSM 5908* was grown in a liquid culture supplemented with erythromycin (50 µg mL^{-1}), and yielded SP-1132 (6.3 mg L^{-1}) and SP-1294 (3.2 mg L^{-1}). Peptides were purified by XAD-16 chromatography and then subjected to preparative HPLC (Nucleosil C18, 5 µm, 250 × 20 mm, Grom, Herrenberg, Germany).

ES-MS and ES-MS/MS experiments were performed on an API III TAGA 6000 E triple-quadrupole mass spectrometer (Perkin – Elmer Sciex, Thornhill, Canada). High-resolution mass spectra were measured on an APEX II FTICR-MS instrument (4.7 T, Bruker Inc., Bremen, Germany) in the positive-ion mode with ES ionization. The resolution was 21 000 (SP-1132) and 65 000 (SP-1294), respectively. NMR spectroscopy experiments

Table 2. ^{1}H and ^{13}C NMR shifts of peptide SP-1294 **4** ([D$_6$]DMSO, 305 K).

	N/C′, δ [ppm]	α, δ [ppm]	β, δ [ppm]	Others, δ [ppm]		
[1]Leu		3.59	1.35	γ: 1.44, δ: 0.76/0.75		
	168.5	50.7	39.6	γ: 23.1, δ: 21.2/22.3		
[2]Cht	8.47	4.48	4.65	OH$^{\gamma}$: 5.58, 2: 7.30, OH^4: 10.00		
	169.2	58.2	71.7	1: 133.6, 2: 128.2, 4: 152.2, 3: 118.9		
				5: 6.84, 6: 7.07		
				5: 115.7, 6: 126.7		
[3]Asn	8.32	4.73	2.58/2.46	δ: 7.35/6.90		
	170.0	49.5	37.1	γ: 171.5		
[4]Hpg	8.04	5.53	–	2: 6.62		
	167.7	54.0	–	2: 114.0, 1: 132.2, 3: 149.0, 4: 144.9		
				5: 7.20, 6: 6.85		
				5: 118.7, 6: 120.4		
[5]Hpg	8.58	5.23	–	2,6: 7.21, 3,5: 6.78, OH^4: 9.56		
	167.7	56.5	–	2,6: 129.4, 3,5: 115.3, 4: 157.1, 1: 126.1		
[6]Cht	6.49	4.61	5.32	OH$^{\gamma}$: 5.55, 2: 7.69		
	167.5	58.4	71.7	1: 140.3, 2: 128.7, 3: 125.0, 4: 149.6		
				5: 7.21, 6: 7.39		
				5: 123.2, 6: 125.1		
[7]Dpg	8.85	5.12	–	2,6: 6.25, OH^{3,5}: 9.33, 4: 6.15		
	171.4	56.0	–	2,6: 105.2, 3,5: 158.3, 4: 102.0, 1: 139.0		
	1′	2′	3′	4′	5′	6′
Gal	5.57	3.85[b]	3.85[b]	3.84[b]	3.97	3.55/3.39
	99.6	69.0[b]	69.0[b]	68.2[b]	72.1	59.9
OH	–	4.49[a]	4.76[a]	4.67[b]	–	4.51

[a] Assignment arbitrary. [b] Assignment ambiguous.

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were carried out on an AMX600 NMR spectrometer (Bruker, Karlsruhe, Germany) equipped a 5 mm triple-resonance probehead with *z*-gradients. Edman degradation was performed on a Hewlett–Packard 241 protein sequencer equipped with a biphasic column detector (Hewlett–Packard, Waldbronn, Germany). For amino acid analysis with GC-MS (HP 5973/HP 6890, Agilent Technologies, Waldbronn, Germany), the peptides were hydrolyzed under vacuum (6 N HCl containing 5% phenol, 110 °C, 24 h) and derivatized with methanol/HCl (2 N, 110 °C, 15 min), trifluoroacetic anhydride (110 °C, 10 min), and then BSTFA/HMDS/pyridine (4:1:4, 80 °C, 30 min; BSTFA = *N,O*-bis(trimethylsilyl) trifluoroacetamide, HMDS = 1,1,1,3,3,3-hexamethyldisilazane), and analyzed by GC-MS on fused silica capillaries (25 m × 0.25 mm) coated with either L-Chirasil-Val or Lipodex E (30%) in PS255 (film thickness $d_f = 0.13$ μm). For sugar analysis, SP-1294 was subjected to methanolysis (HCl (0.65 N) in methanol/methyl acetate (4:1), 70 °C, 16 h). The trimethylsilyl derivatives were prepared by using BSTFA/pyridine (1:1, 80 °C, 30 min), and analyzed by GC-MS on an HP 1-MS fused silica capillary (30 m × 0.25 mm; $d_f = 0.25$ μm, Agilent Technologies).

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New Phosphorus Ligands for the Rhodium-Catalyzed Isomerization/Hydroformylation of Internal Octenes

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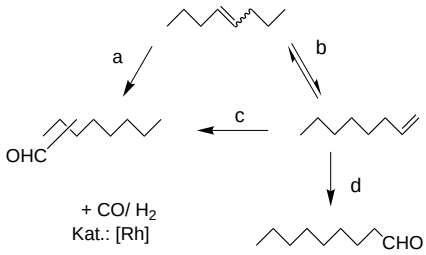
The synthesis of placticizers is closely related to the *n*-regioselective hydroformylation of olefins. World-wide, propene is an important feed stock in the rhodium-catalyzed synthesis of *n*-butanal. The use of higher internal olefins, for example di-*n*-butene from fraction II of the refining process, offers a very interesting and financially attractive alternative that is also used industrially. In these processes the use of unmodified cobalt catalysts and cobalt–phosphane complexes is dominant. At 80–350 bar and 160–190 °C regioselectivities of around 50% with regard to the desired terminal hydroformylation product are achieved, this can be increased to over 80% by modifying the catalyst with a suitable phosphine ligand.[1]

The development of a catalyst that delivers high activities and selectivities under mild conditions is not only of industrial importance, Scheme 1 illuminates the scientific problems with



Scheme 1. Isomerization and hydroformylation of (*Z*)/(*E*)-4-octene.

the example of 4-octene as a substrate. The catalyst and the reaction conditions must be coordinated so that a dynamic kinetic control of the reaction, based on isomerization to the thermodynamically less stable terminal olefin (step b) occurs and that this olefin rapidly undergoes the final *n*-regioselective hydroformylation step (d). The formation of the isomeric aldehydes (a, c) is thus suppressed.

Recently van Leeuwen et al. reported that with xantphos-type diphosphines rhodium catalysts gave *n*-nonanal in 86% regioselectivity from (*E*)-4-octene.[2] The low isomerization activity of the catalyst however, resulted in turnover frequen-

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