Asymmetric *syn*-Dihydroxylation of β-Substituted (2*R*)-*N*-(α,β-Enoyl)bornane-10,2-sultams

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Dedicated to the memory of Professor *Vladimir Prelog*

Variously β-substituted (2*R*)-*N*-[(*E*)-α,β-enoyl]bornane-10,2-sultams were oxidized with OsO_4/4-methylmorpholine 4-oxide in a highly stereoselective manner. In all cases, the attack occurred on the C(α)-*re* face. The absolute configurations of all products were determined by chemical correlation. Mechanistic considerations about the reactive conformation as well as fully refined X-ray crystal structures of the dihydroxylated products are discussed. New neutral conditions for sultam acylation, applicable to the preparation of the taxol and *Taxotere*® C(13) side chain as well as of *Cardizem*® and chloramphenicol precursors, are also presented.

Introduction. – Asymmetric *syn*-dihydroxylation of alkenes provides a powerful tool for the stereocontrolled synthesis of vicinal diols [1]. The practical usefulness of this process has been frequently demonstrated in the syntheses of complex, polyoxygenated compounds [2][2]). Recently, the catalytic version of asymmetric *syn*-dihydroxylation has received much attention because of its efficiency [5]. Although this methodology is well established for (*E*)-olefins, it suffers from several drawbacks when terminal or (*Z*)-configurated unsaturations are considered. On the other hand, the literature offers only few examples of diastereoselective OsO_4 *syn*-dihydroxylation, directed by a chiral auxiliary [6], and the mechanism of this oxidation is still in debate [7].

Results and Discussion. – Some research activities in our laboratories are focused on the synthetic applications of derivatives bearing (2*R*)-bornane-10,2-sultam as a chiral auxiliary [8]. During the studies on the preparation of (2*R*)-*N*-glyoxyloylbornane-10,2-sultam [8a,g], we tested some synthetic pathways, amongst them the oxidative cleavage of diols, obtained by *syn*-dihydroxylation of (2*R*)-*N*-[(*E*)-but-2-enoyl]bornane-10,2-sultam ((−)-**1a**) [9] (see *Scheme*). This reaction was reported to furnish a mixture of unstable and uncharacterized diols, which were immediately converted into their corresponding isopropylidene acetals; the diastereoisomer ratio (9:1) was determined by capillary GC, and their absolute configurations were assigned by chemical correlation [6e]. The same reaction, performed in our laboratories, provided in 80% yield a mixture of crystalline stable diols **2a** and **3a** with 95:5 diastereoselectivity (by ^{1}H-NMR; see *Table 1*) and

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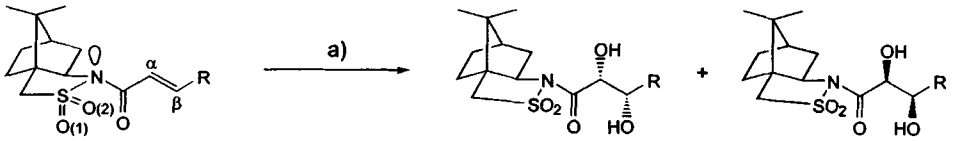
[2]) For $KMnO_4$ oxidation of *N*-enoylbornane-10,2-sultam derivatives, directed towards the synthesis of an *Ionomycin* subunit and *Salinomycin*, see [3] and [4], respectively.

readily separable by column chromatography. The absolute-configuration assignment proposed by *Oppolzer* and *Barras* [6e] was confirmed to be (2′*R*,3′*S*) for **2a** and (2′*S*,3′*R*) for **3a** by X-ray crystal-structure analysis (see *Figs. 1* and *2*).

Scheme



(-)-1a R = Me	(2′*R*,3′*S*)-**2a**	(2′*S*,3′*R*)-**3a**
(-)-1b R = CO_2Me	(2′*R*,3′*R*)-**2b**	(2′*S*,3′*S*)-**3b**
(-)-1c R = C(O)-(2*R*)-bornane-10,2-sultam	(2′*R*,3′*R*)-**2c**	(2′*S*,3′*S*)-**3c**
(-)-1d R = Ph	(2′*R*,3′*S*)-**2d**	(2′*S*,3′*R*)-**3d**
(-)-1e R = 4-$MeOC_6H_4$	(2′*R*,3′*S*)-**2e**	(2′*S*,3′*R*)-**3e**
(-)-1f R = 4-$NO_2C_6H_4$	(2′*R*,3′*S*)-**2f**	(2′*S*,3′*R*)-**3f**

a) 0.3 mol-equiv. of OsO_4, NMO, *t*-BuOH/DMF 1:1

Table 1. *Asymmetric Dihydroxylation of (2R)-N-(α,β-Enoyl)bornane-10,2-sultams* **1**

	Temperature [°]	Time [h]	Yield [%]	Diastereoisomer ratio **2**/**3**	Absolute configuration
(−)-**1a**	−20	5.0	80	95:5	(2′*R*,3′*S*)
(−)-**1b**	20	2.5	84	79:21	(2′*R*,3′*R*)
	0	1.5	78	80:20	(2′*R*,3′*R*)
	−20	20.0	83	85:15	(2′*R*,3′*R*)
(−)-**1c**	20	1.5	79	> 99:1	(2′*R*,3′*R*)
(−)-**1d**	0	4.0	89	95:5	(2′*R*,3′*S*)
	−20	5.0	86	96:4	(2′*R*,3′*S*)
(−)-**1e**	−20	5.0	78	95:5	(2′*R*,3′*S*)
(−)-**1f**	−20	5.0	88	85:15	(2′*R*,3′*S*)

Two major pathways, with several variations, have been proposed for the OsO_4 dihydroxylation process. Based on kinetic considerations [10] as well as absolute configuration predictions [11], *Sharpless* and coworkers privileged a formal [2 + 2] cycloaddition [12] leading to an osmaoxetane intermediate, which in turn rearranges to an osmium(VI) glycolate [13]. This cycloaddition is characterized by a nucleophilic stage during which one O-atom attacks an olefinic C-atom, and an electrophilic stage in which the other olefinic C-atom attacks the Os-atom. In contrast, *Corey* and coworkers proposed a [3 + 2] cycloaddition process [14] in which weak coordination causes sufficient π-electron transfer to the metal to render the coplanar equatorial O-atoms more electron rich and nucleophilic in comparison to the electrophilic axial O-atoms. The transitory [3 + 2] O-axial/O-equatorial cycloadduct thus obtained then rearranges to the thermodynamically more stable O,O-diequatorial osmium(VI)-glycolate intermediate. Alternatively,

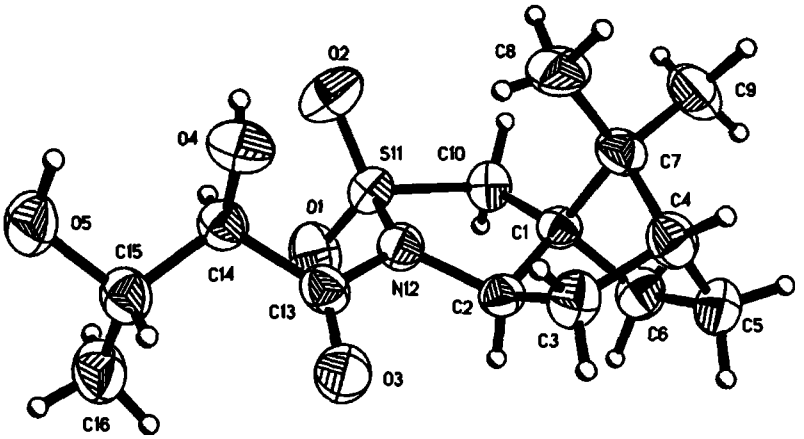


Fig. 1. *ORTEP Diagram of* **2a** *showing the (2'R,3'S)-configuration.* Thermal ellipsoid at 50% probability level; arbitrary numbering.

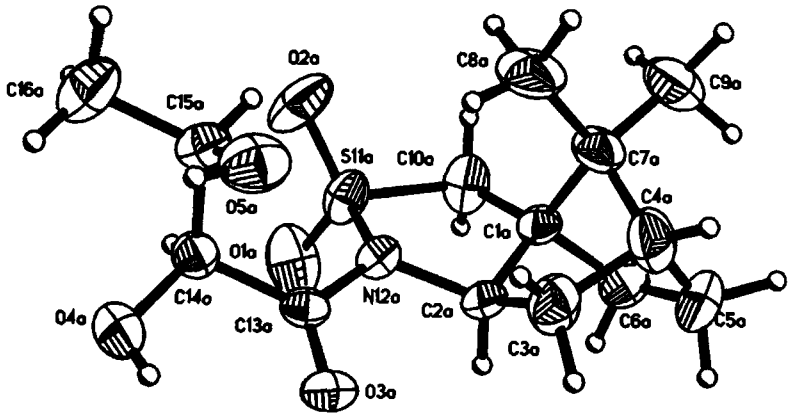


Fig. 2. *ORTEP Diagram of one of the two independent molecules of* **3a** *showing the (2'S,3'R)-configuration.* Thermal ellipsoids at 50% probability level; arbitrary numbering.

this latter intermediate may also be obtained from an initial olefin-Os butterfly π-coordinated complex, after a rapid 90° rotation about the Os–olefin axis. This more direct rationalization predicts well the absolute configuration of the adducts in the asymmetric catalyzed process, and is based on recent X-ray and NMR studies of a highly reactive bidentate [OsO_4(1,2-diamine)] complex [15]. Both concerted [3 + 2] and non-concerted [2 + 2] mechanisms have been discussed in detail [16], but more fundamental to us is the fact that both of them involve nucleophilic attack of one O-atom at the olefin with concomitant electrophilic addition. We earlier reported on the influence of the conformation of *N*-enoylbornane-10,2-sultams on their LUMO, for nucleophilic and cyclo-[4 + 2] additions [17]. We thus were interested to concentrate on the electronic influence of the β-substituent, because the initial work of *Oppolzer* and *Barras* was strictly confined to simple β-alkylated analogues [6e].

The previously unreported (2*R*)-*N*-[(*E*)-3-(methoxycarbonyl)prop-2-enoyl]bornane-10,2-sultam ((−)-**1b**)[3]) was conveniently obtained in 65% yield by acylation of (2*R*)-bornane-10,2-sultam on successive treatment with NaH (1.0 mol-equiv.) and monomethyl ester of fumaroyl chloride (= methyl (*E*)-4-chloro-4-oxobut-2-enoate) [19]. Oxidation of (−)-**1b** (0.3 mol-equiv. of OsO_4, DMF/*t*-BuOH 1:1, 2.0 mol-equiv. of 4-methylmorpholine 4-oxide (NMO) [20]) was much slower at −20° and provided in 83% yield a 85:15 mixture of crystalline diols **2b** and **3b**, separable by column chromatography (*Table 1*). At room temperature, a similar yield and a slightly lower diastereoselectivity were obtained after 2.5 h. The absolute configuration was established by chemical correlation as (2′*R*,3′*R*) for the major product **2b**[4]). This was also confirmed by X-ray analysis of the crystals obtained from i-PrOH (see *Fig. 3*).

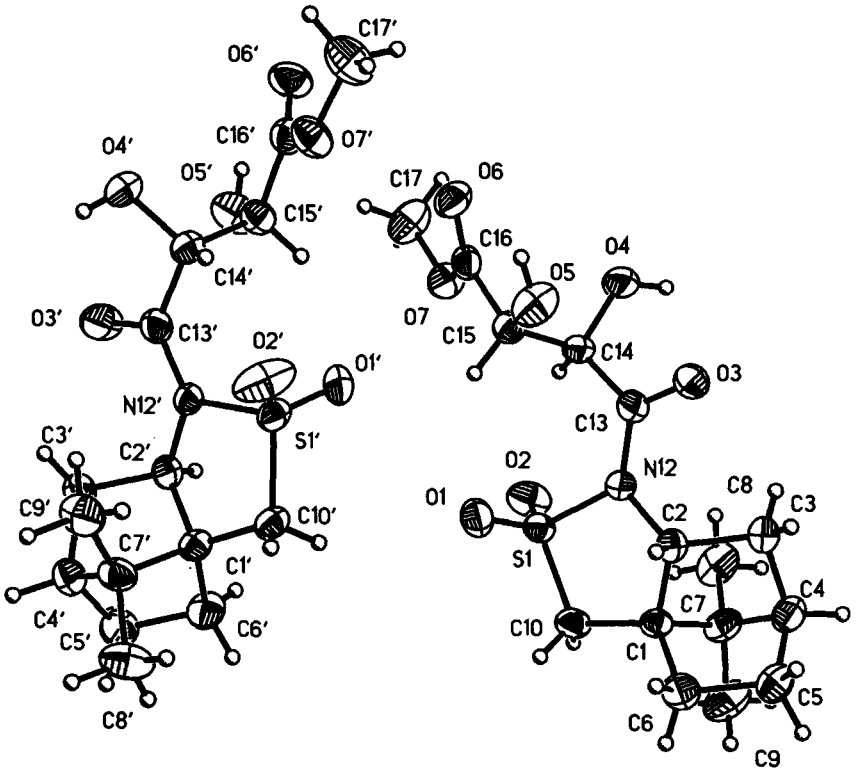


Fig. 3. *ORTEP Diagram of* **2b** *showing two-fold symmetry of the two symmetrically independent molecules and (2′*R*,3′*R*)-configuration.* Thermal ellipsoids at 50% probability level; arbitrary numbering.

Taking advantage of the cooperative effect of two prosthetic groups [22], we obtained, according to ^{1}H-NMR and HPLC analyses, more than 98% de by *syn*-dihydroxylation of the known *N*,*N*′-fumaroylbis[(2*R*)-bornane-10,2-sultam] ((−)-**1c**) [23]. The absolute configuration of diol **2c** was established as (2′*R*,3′*R*) by chemical correla-

[3]) For the corresponding ethyl ester, see [18]; (+)-**1b** was erroneously reported in [18a].

tion[4]) and X-ray analysis of pure single crystals obtained in 79% yield after crystallization from hexane/AcOEt (see *Fig. 4*)[5]).

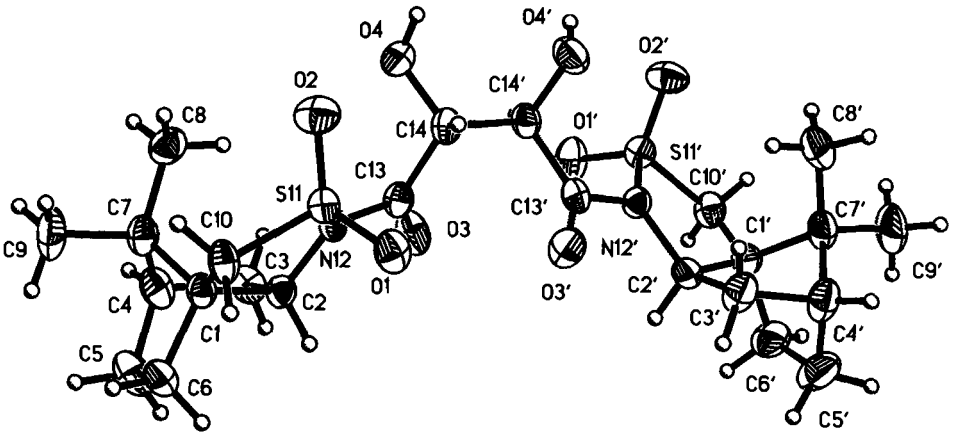


Fig. 4. *ORTEP Diagram of* **2c** *showing (2'*R*,3'*R*)-configuration.* Thermal ellipsoids at 50% probability level; arbitrary numbering.

The known (2*R*)-*N*-cinnamoylbornane-10,2-sultam ((−)-**1d**) [18b][25] was obtained in 87% yield from the free sultam, using novel neutral acylation conditions (1.2 mol-equiv. of cinnamoyl chloride, 1.25 mol-equiv. of AgCN, toluene, 110°)[6]), followed by simple crystallization from EtOH. The glycol was easily formed under the previous oxidation conditions (see above), at −20° with 92% de, and pure material was obtained in 80% yield after simple crystallization from CCl_4. The absolute configuration of **2d** was ascertained by chemical correlation with the known (+)-(2*R*,3*S*)-methyl 2,3-dihydroxy-3-phenylpropanoate [28][7]), thus emphasizing the applicability of this methodol-

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[4]) Protection ($Me_2C(OMe)_2$, Me_2CO, TsOH; 89–95% [6e]), followed by saponification according to the well-established methodology (1.5 mol-equiv. of LiOH, THF/H_2O 5:2; 88–95% [9]) gave, after acid-base extraction and esterification (CH_2N_2, Et_2O; 85–90%), the recovered (−)-(2*R*)-bornane-10,2-sultam (81–90%), beside (−)-(2*R*,3*R*)-dimethyl 2,3-*O*-isopropylidenetartrate (65–81%; $[\alpha]_D = -45.5$ ($c = 1.28$, $CHCl_3$); [21]: $[\alpha]_D = -42.6$ ($c = 5.1$, $CHCl_3$)).

[5]) The oxidation proceeded with the same topicity but much faster using the more reactive RuO_4 catalyst (0.07 mol-equiv. of $RuCl_3$, 0.22M in H_2O; 1.5 mol-equiv. of $NaIO_4$, 0.24M in H_2O; AcOEt/MeCN 1:1, 0.1 mmol/ml; 0°; 15–20 min [24]) on (−)-**1b** (74%; 44% de) and (−)-**1c** (65%; > 98% de). Unfortunately, considerable amounts of by-products originated after prolonged time under these conditions.

[6]) These conditions were earlier used for esterification of alcohols [26]. For alternative neutral acylation conditions of free or Me_3Si-protected bornane-10,2-sultams, see [6e] and [27], respectively.

[7]) Saponification (LiOH, THF/H_2O 5:2; 94% [9]) gave, after acid-base extraction and esterification (CH_2N_2, Et_2O; 91%), the recovered (−)-(2*R*)-bornane-10,2-sultam (89%), beside (+)-(2*R*,3*S*)-methyl 2,3-dihydroxy-3-phenylpropanoate (81%; $[\alpha]_D = +11.5$ ($c = 1.08$, $CHCl_3$); [29]: $[\alpha]_D = -10.7$ ($c = 1.1$, $CHCl_3$) for the enantiomer). Similarly, (+)-(2*R*,3*S*)-methyl 2,3-dihydroxy-3-(4-methoxyphenyl)propanoate (83%; $[\alpha]_D = +6.3$ ($c = 0.8$, $CHCl_3$); [30]: $[\alpha]_D = -4.62$ ($c = 1.87$, $CHCl_3$) for the enantiomer) was obtained from (2'*R*,3'*S*)-**2e**. (+)-(2*R*,3*S*)-Ethyl 2,3-dihydroxy-3-(4-nitrophenyl)propanoate (80%; $[\alpha]_D = +9.3$ ($c = 0.51$, $CHCl_3$); [31]: $[\alpha]_D = -8.9$ ($c = 0.8$, $CHCl_3$) for the enantiomer) was obtained after appropriate saponification/esterification (*1.5 mol-equiv. of EtOH, 1.5 mol-equiv. of DCC, 0.01 mol-equiv. of 4-(dimethylamino)pyridine* (DMAP), CH_2Cl_2) from (2'*R*,3'*S*)-**2f**.

ogy for the synthesis of the C(13) side chain of taxol and *Taxotere*® anti-cancer analogues [29][32]. The 4-methoxy- and 4-nitrocinnamoyl analogues (−)-**1e,f** were similarly synthesized under these neutral conditions in 93 and 77% isolated yield, respectively, after crystallization from EtOH. They both exhibited identical topicity[7]) during their *syn*-dihydroxylation at −20° with 90 and 70% de, respectively. Pure (2′*R*,3′*S*)-**2e,f** could be obtained after crystallization from EtOH and toluene in 65 and 51% yield, respectively.

By introducing an electron-withdrawing group at C(*β*) of (−)-**1a**, we lowered both the LUMO and HOMO of the olefin moiety of (−)-**1a**, thus decreasing the rate of the electrophilic step in the case of (−)-**1b,c**, and, consequently, requiring a higher temperature to reach a similar conversion time (see *Table 1*). More interestingly, for *N*-cinnamoylsultam (−)-**1d**, the conjugated aromatic substituent decreased the LUMO and increased the HOMO levels of the reactive double bond, thus favoring both nucleophilic and electrophilic interactions (see *Table 2*)[8]). When compared with (−)-**1d**, these two MOs are shifted towards higher or lower energies, respectively, when (−)-**1e,f** are considered, and thus well explain their relative reactivities, as expressed by the respective isolated yields.

Table 2. *PM3-Calculated Geometrical, Conformational, and Electronic Parameters of (−)-***1a**–**f** [17]

	Conformational energy [kcal/mol]	HOMO [eV]	LUMO [eV]	*Δh*N [Å]	Atomic coeff. C(α)-*re*		Atomic coeff. C(α)-*si*	
					C(α)	C(*β*)	C(α)	C(*β*)
(−)-**1a** *anti*-s-*cis*	−102.8	−10.23	−0.56	0.123	0.030	−0.035	−0.050	0.045
syn-s-*cis*	−101.2	−10.20	−0.41	0.119	0.080	−0.060	−0.050	0.055
(−)-**1b** *anti*-s-*cis*	−173.3	−10.45	−0.86	0.148	0.230	−0.205	−0.235	0.225
syn-s-*cis*	−172.9	−10.42	−0.98	0.114	0.260	*−0.240*	−0.230	*0.255*
(−)-**1c** *anti*-s-*cis*	−197.1	−10.33	−0.78	0.145	0.201	−0.190	−0.206	0.195
syn-s-*cis*	−196.9	−10.42	−0.98	0.114	0.260	−0.255	−0.240	0.235
(−)-**1d** *anti*-s-*cis*	−69.9	−9.34	−0.71	0.150	0.193	−0.185	−0.195	0.196
syn-s-*cis*	−68.4	−9.53	−0.85	0.119	0.200	−0.206	−0.195	0.198
(−)-**1e** *anti*-s-*cis*	−108.3	−8.93	−0.67	0.154	0.185	−0.190	−0.175	0.200
syn-s-*cis*	−106.6	−9.12	−0.80	0.124	0.208	−0.210	−0.204	0.196
(−)-**1f** *anti*-s-*cis*	−78.1	−10.13	−1.62	0.147	0.180	−0.130	−0.176	0.135
syn-s-*cis*	−76.2	−10.32	−1.80	0.119	0.175	−0.140	−0.170	0.128

[8]) The PM3 parameters for Os are actually not available [33]. The LUMO energy of OsO_4 was earlier measured by photoelectron spectroscopy [34], or calculated by *ab initio* methods [16], but is of poor utility, since mono- or dicoordination to OsO_4 is known to deform the tetragonal geometry to a trigonal or square bipyramidal complex, with substantial increase of its HOMO energy as well as decrease of its LUMO level [16]. This enhances both the nucleophilic and electrophilic characters of the complex and, *e.g.*, explains the higher reactivity observed in the presence of complexing amines [15].

The constant C(α)-*re*-face attack observed during this process is consistent with the steric model of *Kim* and *Curran* [35], invoking the thermodynamically more stable SO_2/C=O *anti*, C=O/C=C s-*cis* conformer of (−)-**1a**–**f** (see *Table 2*). *Oppolzer* and *Barras* earlier proposed the sterically less hindered C(α)-*re* approach on the *syn*-s-*cis* conformer, supposedly constrained by chelation with OsO_4 [6e][36]. A substrate such as (−)-**2c** would require three molecules of Os per oxidation event, which seems unlikely in a system which is catalytic in metal. Furthermore, with respect to the poor O-atom chelating properties of OsO_4, especially in a solvent system such as DMF/*t*-BuOH 1:1, we propose that this thermodynamically less stable conformer may participate in the overall stereochemical course of the reaction by virtue of its high reactivity. This reactivity results from two effects, as earlier proposed [17]. Firstly, the better delocalization of the π-electronic system toward the SO_2 moiety, due to the higher planarity of the N-atom (see *Table 2*). This planarity results from geometrical minimization of steric, dipole-dipole, and electrostatic interactions between the SO_2 and C=O groups, and the electronically ideal alignment of the S–N–C=O dihedral angle [17]. This is reflected by the larger LUMO C(α)-C(β) atomic coefficients, calculated for the *syn*-s-*cis* conformers of (−)-**1a**–**e**, as well as by the lower energy level of the LUMO for the *syn*-s-*cis* conformers of (−)-**1b**–**f** (see *Table 2*) [17].

Secondly, this reactivity is also due to the cooperative steric and stereoelectronic effects of this conformation, generated by the stereoelectronic influence of the lone electron pair at the N-atom, itself hypothetically directed and stabilized by an anomeric effect of the *anti*-periplanar S=O(1) bond [8d][17][37][9]). It is noteworthy to mention that (−)-**1b** is the first example reported to date [17], where PM3 calculations suggest a systematic mismatching of the stereoelectronic influence of the C(β) atom with the steric effect, in both SO_2/C=O *syn*- and *anti*-periplanar conformations [17]. Indeed, in this case, the C(β) atomic coefficient (−0.240) is smaller on the C(α)-*re* face than that of the C(α)-*si* face (0.255), in the *syn*-s-*cis* conformation. Furthermore, the smaller atomic coefficient on the C(β) atom of (−)-**1f**, when compared with (−)-**1d,e**, may hypothetically explain the reduced influence of the stereoelectronic effect in that case. This may tentatively rationalize the lower diastereoselectivities observed for (−)-**1b,f**.

These features are also illustrated by the X-ray crystal-structure analyses of **2a**–**c** and **3a**, which were effected during an investigation of the polyoxygenated *N*-acylated bor-

[9]) This hypothesis is also reinforced by a recent new bornane-3,2-sultam [38], characterized by a sp^3 trisubstituted C(α)-SO_2, which obliges both S=O bonds to adopt a staggered conformation, resulting in a S=O(2) pseudoaxial orientation [17]. Consequently, the pyramidalization of the N-atom is inverted in order to profit from the *anti*-periplanar anomeric stabilization of the N lone electron pair. According to *Curran*'s hypothesis [35], attack on the *anti*-s-*cis* conformer should be sterically influenced by the SO_2 moiety. In contrast, approach on the highly reactive *syn*-s-*cis* conformer would be directed by the non-stereogenic C(α)-N center. This latter participation better explains the absence of diastereoselectivity observed during the noncatalyzed [4 + 2] cycloaddition reported. Under chelating *Lewis* acid conditions [39], a more detailed discussion of the influence of O(1)/O(2) sites of coordination, as well as s-*cis*/s-*trans* equilibria, excess of *Lewis* acid, and stereoelectronic cooperation of the N lone electron pair should be developed. It is also worthwhile to note that Chinese authors have unfortunately erroneously assigned the absolute configuration of the main cycloadducts in entries 4 and 7 of their publication [38].

nane-10,2-sultams derivatives[10]). Although we have not found any intramolecular SO_2/OH H-bond in these four structures [37], several other aspects, presented in *Table 3*, are worthy of mention. First of all, two very similar independent structures were observed in **2b** and **3a**. As we earlier reported, the planarity of the N-atom correlates well with the amplitude of the S–N–C(13)–O(3) dihedral angle. To the best of our knowledge, **2b** possesses the largest S–N–C(13)–O(3) torsional angle (172.4°) and the smallest ΔhN (0.112 Å) ever reported in this series [17] for a SO_2/C=O *anti*-periplanar conformation[11]). The pyramidalization of **2b** is nevertheless still more pronounced than that observed for a *syn*-periplanar conformation[10]). As we also remarked earlier [37], the hypothetical anomeric effect between the N lone electron pair and the S=O(1) bond is not systematically translated by the elongation of the S=O(1) *vs.* S=O(2) bond lengths, as shown, *e.g.*, by **2b′,c**.

Table 3. *Selected Bond Lengths* [Å] *and Dihedral Angles* [°] *for* **2a–c** *and* **3a**

	2a	**2b**	**2b′**	**2c**	**3a**	**3a′**
S–O(1)	1.425(3)	1.432(4)	1.400(4)	1.418(3)	1.430(3)	1.434(3)
S–O(2)	1.422(3)	1.406(4)	1.449(4)	1.427(3)	1.424(3)	1.425(3)
S–N	1.691(3)	1.724(4)	1.678(3)	1.689(3)	1.685(2)	1.686(2)
ΔhN	0.234(4)	0.112(4)	0.137(4)	0.171(3)	0.219(3)	0.217(3)
S–N–C(13)–O(3)	146.0(3)	170.8(4)	172.4(5)	156.5(3)	148.6(2)	148.5(2)
O(1)–S–N–C(2)	95.6(2)	95.6(3)	97.0(4)	94.9(3)	96.9(2)	96.7(2)
O(2)–S–N–C(2)	−134.5(2)	−136.4(3)	−135.6(4)	−135.5(2)	−134.6(2)	−134.4(2)
S–N–C(2)–C(3)	146.7(2)	146.2(4)	147.1(3)	147.3(3)	146.4(2)	146.5(2)
O(1)–S–N–lp[a])	−161.5(3)	−168.2(4)	−166.0(4)	−165.4(3)	−160.7(3)	−160.9(3)
O(2)–S–N–lp[a])	− 31.3(4)	− 40.2(4)	− 38.6(5)	− 35.8(3)	− 32.2(3)	− 32.1(3)

[a]) lp = lone electron pair.

Conclusion. – Although we invoke two nucleophilic-electrophilic steps, the dichotomy between the concerted/non-concerted mechanism still remains open, as our results do not exclude the [3 + 2] cycloaddition pathway [41], but propose the possible influence of the reactive *syn*-s-*cis* conformer. The asymmetric *syn*-dihydroxylation described herein exemplifies the electronic influence of the β-substituent as well as the utility of the bornane-10,2-sultam auxiliary, available in both antipodal forms, for the synthesis of enantiomerically pure vicinal diols. The value of this methodology is exemplified by the preparation of pure **2d–f** as potential intermediates for the synthesis of enantiomerically pure paclitaxel and docetaxel C(13) side chains [42], the cardiac drug (+)-diltiazem [43], and the antibiotic (−)-chloramphenicol [31] as well as – by suitable substitution of the aromatic moiety – the leukotriene antagonist SKF 104353 [44], and antibiotics such as

[10]) For the first and unique example of an X-ray crystal structure of unchelated *N*-acylated bornane-10,2-sultam derivative, exhibiting a SO_2/C=O *syn*-periplanar conformation, and possessing a practically planar N-atom (ΔhN = 0.083 Å), see [37].

[11]) For an other extreme *anti*-periplanar *N*-acylbornane-10,2-sultam (S–N–C=O 172.4°, ΔhN = 0.164 Å), see [40].

vancomycin, thiamphenicol, and florfenicol [45]. Further studies directed towards the asymmetric *syn*-dihydroxylation as well as the aminohydroxylation [46] of (2*R*)-*N*-enoylbornane-10,2-sultam derivatives are now in progress in our laboratories.

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Experimental Part

General. All reactions with acyl chlorides were carried out under Ar with anh. solvents, dried according to standard procedures. Flash column chromatography (FC): according to [47]; silica gel *60* (*Merck*, 200–400 mesh). TLC: *Merck* aluminium plates (silica gel *60* F_{254}); visualization with a soln. of MoO_3 and $Ce_2(SO_4)_3$ in 15% H_2SO_4/H_2O. M.p.: *Kofler* hot-stage apparatus; uncorrected. Optical rotations: *JASCO-DIP-360* polarimeter with a 20° thermally jacketed 10-cm cell. IR Spectra: *Perkin-Elmer 1640* FT-IR; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker Am-500* (500 and 125 MHz) and *Varian Gemini* (200 and 50 MHz) spectrometers using residual $CHCl_3$ as internal reference; δ in ppm J in Hz.

X-Ray Crystal-Structure Determination of Compounds **2a–c** *and* **3a**. Crystal data and measurement conditions are given in *Table 4*. Diffraction data were collected at r.t. on a four-circle *Enraf-Nonius-MACH3* diffractometer. Monochromated CuK_α radiation (λ 1.54178 Å) was applied, and ω-2θ scan technique was used during measurements. The structures were solved by the SHELXS [48] and refined with the SHELXL [49] programs. Positions for hydroxy H-atoms were found from the $\Delta\rho$ maps and refined. Remaining H-atoms were placed at geometrical positions and refined in riding mode. Crystallographic data for **2a–c** and **3**, have been deposited at the *Cambridge Crystallographic Data Center*.

*(–)-(2R)-*N*-[(E)-3-(Methoxycarbonyl)prop-2-enoyl]bornane-10,2-sultam* (= *(–)-Methyl (E)-4-[(3aS,6R,7aR)-1,4,5,6,7,7a-Hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazol-1-yl]-4-oxobut-2-enoate* S,S-*Dioxide*; (–)-**1b**). To a stirred suspension of NaH (225 mg; 4.52 mmol; 50% in mineral oil, washed 3 times with dry pentane) in dry toluene (35 ml) was added (2*R*)-bornane-10,2-sultam (972 mg, 4.52 mmol) in toluene (15 ml). After 30 min at r.t., freshly distilled methyl (*E*)-4-chloro-4-oxobut-2-enoate (669 mg, 5.15 mmol) in toluene (15 ml) was added dropwise, and the mixture was stirred at r.t. for 2 h. The reaction was quenched by addition of sat. aq. NH_4Cl soln. (40 ml) and extracted with CH_2Cl_2 (4 × 20 ml). The org. phase was dried ($MgSO_4$) and evaporated and the residue purified by CC (hexane/AcOEt 8:2): pure (–)-**1b** (65%). White solid, M.p. 126–128° (hexane/AcOEt); $[\alpha]_D = -104.9$ (c = 1.19, $CHCl_3$). IR: 3433, 3068, 2960, 2883, 1726, 1679, 1636, 1458, 1432, 1369, 1334, 1303, 1276, 1169, 1135, 1065, 981, 771. ^1H-NMR: 7.55 (*d*, J = 15.3, 1 H); 6.91 (*d*, J = 15.3, 1 H); 3.96 (*dd*, J = 6.0, 6.8, 1 H); 3.81 (*s*, 3 H); 3.57 (*d*, J = 13.9, 1 H); 3.47 (*d*, J = 13.9, 1 H); 2.18–2.10 (*m*, 2 H); 2.00–1.82 (*m*, 3 H); 1.52–1.29 (*m*, 2 H); 1.17 (*s*, 3 H); 0.99 (*s*, 3 H). ^{13}C-NMR: 165.0 (MeO*O*C); 162.4 (C(1')); 133.6 (C(2')); 132.3 (C(3')); 65.1 (C(2)); 53.0 (MeO); 52.3 (C(10)); 48.7 (C(1)); 47.8 (C(7)); 44.6 (C(4)); 38.2 (C(3)); 32.8 (C(6)); 26.4 (C(5)); 20.8 (C(8)); 19.8 (C(9)). EI-MS: 327 (M^+), 296 ([M – OMe]$^+$). HR-MS: 327.11449 ($C_{15}H_{21}NO_5S^+$, M^+; calc. 327.11405).

*(–)-*N,N'*-Fumaroylbis[(2R)-bornane-10,2-sultam]* (= *(–)-1,1'-[(E)-1,4-Dioxobut-2-ene-1,4-diyl]bis-[(3aS,6R,7aR)-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazole] 2,2,2',2'-Tetraoxide*; (–)-**1c**). For synthesis and analyses, see [23]. MS: 510 (0, $M^{+\cdot}$), 431 (1), 296 (45), 268 (10), 231(28), 204 (22), 150 (32), 135 (100), 107 (33), 93 (42), 82 (24), 67 (12).

*(–)-(2R)-*N*-Cinnamoylbornane-10,2-sultam* (= *(–)-(3aS,6R,7aR)-1,4,5,6,7,7a-Hexahydro-8,8-dimethyl-1-[(E)-1-oxo-3-phenylprop-2-enyl]-3*H*-3a,6-methano[2,1]benzisothiazole 2,2-Dioxide*; (–)-**1d**). A suspension of AgCN (168 mg, 1.25 mmol), cinnamoyl chloride (= (*E*)-3-phenylprop-2-enoylchloride; 200 mg, 1.2 mmol) and (2*R*)-bornane-10,2-sultam (215 mg, 1.0 mmol) in toluene (5 ml) was refluxed for 8 h. The cold soln., diluted with AcOEt (2 × 20 ml), was filtered through *Celite*. The filtrate was evaporated and the residue crystallized from EtOH to give pure (–)-**1d** (87%). White solid. M.p. 189–190°. $[\alpha]_D = -94.9$ (c = 1.10, $CHCl_3$). For analyses, see [18b].

*(–)-(2R)-*N*-(4-Methoxycinnamoyl)bornane-10,2-sultam* (= *(–)-(3aS,6R,7aR)-1,4,5,6,7,7a-Hexahydro-1-[(E)-3-(4-methoxyphenyl)-1-oxoprop-2-enyl]-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazole 2,2-Dioxide*; (–)-**1e**). Obtained in 93% yield from (2*R*)-bornane-10,2-sultam and 4-methoxycinnamoyl chloride, as described for (–)-**1d**. White solid. M.p. 148–150° (EtOH). $[\alpha]_D = -94.9$ (c = 0.78, $CHCl_3$). IR: 3020, 2960, 1670, 1600, 1570, 1510, 1330, 1290, 1260, 1205, 1175, 1130, 1110, 1030, 990. ^1H-NMR: 7.76 (*d*, J = 16, 1 H); 7.54 (*m*, 2 H); 7.04 (*d*, J = 16, 1 H); 6.5 (*m*, 2 H); 4.0 (*dd*, J = 5, 7, 1 H); 3.83 (*s*, 3 H); 3.55 (*d*, J = 14, 1 H); 3.46 (*d*, J = 14, 1 H); 2.17 (*m*, 2 H); 1.90 (*m*, 3 H); 1.3–1.6 (*m*, 2 H); 1.21 (*s*, 3 H); 0.99 (*s*, 3 H). ^{13}C-NMR: 164.5 (C(1')); 161.7 (C_p); 145.3 (C(3')); 130.4 (2 C_o); 127.1 (C_{ipso}); 114.9 (C(2')); 114.3 (2 C_m); 65.2 (C(2)); 55.4 (MeO); 53.2 (C(10)); 48.5

Table 4. *Crystal Data and Structure Refinement of Compounds* **2a–c** *and* **3a**

	2a	**3a**	**2b**	**2c**
Empirical formula	$C_{14}H_{23}NO_5S$	$C_{14}H_{23}NO_5S$	$C_{15}H_{23}NO_7S$	$C_{24}H_{36}N_2O_8S_2$
Formula weight	317.39	317.39	361.40	544.67
Crystal system	monoclinic	monoclinic	triclinic	orthorombic
Space group	$P2_1$	$P2_1$	$P1$	$P2_12_12_1$
Until-cell dimensions a [Å]	9.2340(10)	7.0310(10)	7.779(2)	14.029(3)
b [Å]	7.9490(10)	9.1400(10)	7.959(2)	15.263(3)
c [Å]	10.9080(10)	23.939(2)	14.167(3)	12.113(2)
α [°]			99.95(3)	
β [°]	101.930(10)	90.030(10)	99.54(3)	
γ [°]			93.92(3)	
Volume [Å^{-3}]	783.4(2)	1538.4(3)	855.1(4)	2593.7(9)
Z	2	4	2	4
Density calc. [Mg m^{-3}]	1.346	1.370	1.404	1.395
Absorption coeff. [mm^{-1}]	2.026	2.064	2.019	2.298
$F(000)$	340	680	384	1160
Crystal size [mm]	0.14 × 0.14 × 0.21	0.21 × 0.21 × 0.14	0.17 × 0.14 × 0.3	0.14 × 0.21 × 0.14
θ-Range [°]	4.14 to 74.84	3.69 to 74.85	3.19 to 72.16	4.28 to 61.42
	$-11 \le h \le 11$	$-8 \le h \le 8$	$-9 \le h \le 9$	$-15 \le h \le 0$
Index ranges	$-9 \le k \le 0$	$-0 \le k \le 11$	$-9 \le k \le 0$	$-16 \le k \le 0$
	$0 \le l \le 13$	$0 \le l \le 26$	$-16 \le l \le 15$	$0 \le l \le 13$
Refl. collected	1718	3180	2804	1905
	1718	3180	2804	1905
Independent refl.	(R(int) = 0.0000)	(R(int) = 0.0000)	(R(int) = 0.0000)	(R(int) = 0.0000)
Data, restraints, params.	1718, 0, 282	3180, 1, 382	2801, 3, 480	1905, 0, 374
G–O–F on F^2	1.036	1.004	0.960	1.073
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0373$, $wR_2 = 0.1028$	$R_1 = 0.0369$, $wR_2 = 0.0996$	$R_1 = 0.0398$, $wR_2 = 0.1057$	$R_1 = 0.0319$, $wR_2 = 0.0821$
R indices (all data)	$R_1 = 0.0374$, $wR_2 = 0.1029$	$R_1 = 0.0371$, $wR_2 = 0.0999$	$R_1 = 0.0402$, $wR_2 = 0.1108$	$R_1 = 0.0322$, $wR_2 = 0.0824$
Flack parameter	0.00 (2)	0.01 (2)	0.01 (2)	0.04 (2)
Extinction coeff.	0.000 (2)	0.0016 (3)	0.0092 (12)	0.0036 (3)
$\Delta\rho$ [eÅ^{-3}]	0.400 and −0.298	0.297 and −0.346	0.360 and −0.329	0.242 and −0.251

(C(1)); 47.8 (C(7)); 44.7 (C(4)); 38.6 (C(3)); 32.8 (C(6)); 26.5 (C(5)); 20.9 (C(8)); 19.9 (C(9)). MS: 375 (8, $M^{+\cdot}$), 162 (20), 161 (100), 133 (13), 118 (5), 77 (5), 43 (5).

*(−)-(2*R*)-*N*-(4-Nitrocinnamoyl)bornane-10,2-sultam* (= *(−)-(3a*S*,6*R*,7a*R*)-1,4,5,6,7,7a-Hexahydro-8,8-dimethyl-1-[(*E*)-3-(4-nitrophenyl)-1-oxoprop-2-enyl]-3*H*-3a,6-methano[2,1]benzisothiazole 2,2-Dioxide*; (−)-**1f**). Obtained in 77% yield from (2*R*)-bornane-10,2-sultam and 4-nitrocinnamoyl chloride, as described for (−)-**1d**. White solid. M.p. 240–242° (EtOH). $[\alpha]_D = -97.1$ ($c = 0.85$, $CHCl_3$). IR: 3000, 2960, 1670, 1620, 1600, 1515, 1315, 1115, 837. ^{1}H-NMR: 8.22 (*m*, 2 H); 7.78 (*d*, $J = 16$, 1 H); 7.66 (*m*, 2 H); 7.28 (*d*, $J = 16$, 1 H); 4.0 (*t*, $J = 7$, 1 H); 3.59 (*d*, $J = 14$, 1 H); 3.49 (*d*, $J = 14$, 1 H); 2.17 (*m*, 2 H); 1.93 (*m*, 3 H); 1.3–1.6 (*m*, 2 H); 1.20 (*s*, 3 H); 1.00 (*s*, 3 H). ^{13}C-NMR: 163.3 (C(1′)); 148.6 (C_p); 142.3 (C(3′)); 140.3 (C_{ipso}); 129.1 (2 C_o); 124.1 (2 C_m); 121.5 (C(2′)); 65.3 (C(2)); 53.1 (C(10)); 48.7 (C(1)); 47.9 (C(7)); 44.6 (C(4)); 38.4 (C(3)); 32.8 (C(6)); 26.5 (C(5)); 20.8 (C(8)); 19.9 (C(9)). MS: 390 (4, $M^{+\cdot}$), 326 (6), 283 (8), 177 (13), 176 (100), 130 (16), 102 (10), 43 (13).

General Procedure for the OsO_4-Catalyzed syn*-Dihydroxylation of Olefins (−)-***1a–f**. The olefin (1.0 mmol) and 4-methylmorpholine 4-oxide (2.0 mmol) were dissolved in *t*-BuOH/DMF 1:1 (10 ml). OsO_4 (0.3 mmol, 0.05M in *t*-BuOH) was added and the reaction followed by TLC (hexane/AcOEt 7:3). After disappearance of the starting material, the reaction was quenched by addition of a sat. aq. $Na_2S_2O_3$ soln. and the mixture extracted 4× with AcOEt. The combined org. extracts were dried ($MgSO_4$) and evaporated, and the residue was purified by CC (hexane/AcOEt 9:1 → 1:9) or crystallization. For details concerning yields, temp. and reaction times, see *Table 1*.

*(2*R*)-*N*-[(2′*R*,3′*S*)-2′,3′-Dihydroxybutanoyl]bornane-10,2-sultam* (= *(3a*S*,6*R*,7a*R*)-1-[(2*R*,3*S*)-2,3-Dihydroxy-*

*1-oxobutyl]-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazole 2,2-Dioxide*; (2′*R*,3′*S*)-**2a**): White crystals. M.p. 116–118° (hexane/AcOEt). $[\alpha]_D = -112.2$ (*c* = 3.83, MeOH). IR: 3495, 3224, 2965, 2898, 1700, 1460, 1392, 1323, 1266, 1133, 1046, 999, 862, 762, 617. ^{1}H-NMR: 4.39 (*dd*, *J* = 2.8, 7.5, 1 H); 4.25 (*dd*, *J* = 2.8, 6.4, 1 H); 3.94 (*dd*, *J* = 4.9, 7.9, 1 H); 3.56 (br. *s*, OH); 3.56 (*d*, *J* = 13.8, 1 H); 3.45 (*d*, *J* = 13.8, 1 H); 2.73 (br. *s*, OH); 2.21 (*ddd*, *J* = 4.9, 14.0, 8.3, 1 H); 2.08 (*dd*, *J* = 7.9, 14.0, 1 H); 1.98–1.85 (*m*, 3 H); 1.47–1.32 (*m*, 2 H); 1.28 (*d*, *J* = 6.4, 3 H); 1.16 (*s*, 3 H); 0.98 (*s*, 3 H). ^{13}C-NMR: 171.7 (C(1′)); 73.2 (C(2′)); 66.8 (C(3′)); 65.2 (C(2)); 52.8 (C(10)); 49.1 (C(1)); 47.8 (C(7)); 44.5 (C(4)); 38.0 (C(3)); 32.8 (C(6)); 26.4 (C(5)); 20.7 (C(8)); 19.8 (C(9)); 18.7 (C(4′)). EI-MS: 318 ([*M* + H]$^+$), 302 ([*M* − Me]$^+$). HR-MS: 318.1372 ($C_{14}H_{24}NO_5S^+$, [*M* + H]$^+$, calc. 318.1375).

*(2*R*)-*N*-[(2′*S*,3′*R*)-2′,3′-Dihydroxybutanoyl]bornane-10,2-sultam* ((2′*S*,3′*R*)-**3a**): White crystals. M.p. 145–147° (hexane/AcOEt). $[\alpha]_D = -101.8$ (*c* = 1.63, MeOH). IR: 3557, 3496, 2976, 2887, 1689, 1318, 1295, 1219, 1139, 1134, 1112, 1058, 1004, 845, 762, 696, 649, 618. ^{1}H-NMR: 4.57 (*d*, *J* = 1.9, 1 H); 4.21 (*ddd*, *J* = 1.9, 6.4, 12.8, 1 H); 3.94 (*t*, *J* = 6.4, 1 H); 3.52 (br, *s*, OH); 3.53 (*d*, *J* = 13.8, 1 H); 3.43 (*d*, *J* = 13.8, 1 H); 3.11 (br. *s*, OH); 2.10–2.06 (*m*, 2 H); 1.94–1.87 (*m*, 3 H); 1.49–1.44 (*m*, 2 H); 1.33 (*d*, *J* = 6.4, 3 H); 1.15 (*s*, 3 H); 0.98 (*s*, 3 H). ^{13}C-NMR: 173.3 (C(1′)); 74.6 (C(2′)); 69.4 (C(3′)); 64.9 (C(2)); 52.9 (C(10)); 49.1 (C(1)); 47.9 (C(7)); 44.4 (C(4)); 37.9 (C(3)); 32.6 (C(6)); 26.5 (C(5)); 20.4 (C(8)); 19.9 (C(9)); 19.9 (C(4′)). EI-MS: 318 ([*M* + H]$^+$), 302 ([*M* − Me]$^+$). HR-MS: 318.1375 ($C_{14}H_{24}NO_5S^+$, [*M* + H]$^+$; calc. 318.1375).

*(2*R*)-*N*-[(2′*R*,3′*R*)-2′,3′-Dihydroxy-3′-(methoxycarbonyl)propanoyl]bornane-10,2-sultam* (= *Methyl (2*R*,3*R*)-4-[(3a*S*,6*R*,7a*R*)-1,4,5,6,7,7a-Hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazol-1-yl]-2,3-dihydroxy-4-oxobutanoate* S,S-*Dioxide*; (2′*R*,3′*R*)-**2b**): White solid. M.p. 144–146° (hexane/AcOEt). $[\alpha]_D = -98.1$ (*c* = 1.63, $CHCl_3$). IR: 3499, 2997, 2960, 1741, 1684, 1338, 1289, 1243, 1109, 1055, 774, 610. ^{1}H-NMR: 5.03 (br. *s*, 1 H); 4.89 (*d*, *J* = 1.7, 1 H); 3.99 (*dd*, *J* = 5.1, 7.9, 1 H); 3.86 (*s*, 3 H); 3.70 (br. *s*, OH); 3.56 (*d*, *J* = 13.8, 1 H); 3.48 (*d*, *J* = 13.8, 1 H); 3.20 (br. *s*, OH); 2.37–2.22 (*m*, 1 H); 2.11 (*dd*, *J* = 7.9, 14.0, 1 H); 1.98–1.83 (*m*, 3 H); 1.52–1.22 (*m*, 2 H); 1.15 (*s*, 3 H); 0.98 (*s*, 3 H). ^{13}C-NMR: 172.2 (MeO*OC*); 169.7 (C(1′)); 71.6 (C(2′)); 70.8 (C(3′)); 65.8 (C(2)); 53.2 (MeO); 52.8 (C(10)); 49.3 (C(1)); 47.9 (C(7)); 44.4 (C(4)); 38.0 (C(3)); 32.8 (C(6)); 26.3 (C(5)); 20.7 (C(8)); 19.9 (C(9)). EI-MS: 362 ([*M* + H]$^+$), 302 ([*M* − CO_2Me]$^+$). HR-MS: 362.12781 ($C_{13}H_{24}NO_7S^+$, [*M* + H]$^+$; calc. 362.12735).

*(2*R*)-*N*-[(2′*S*,3′*S*)-2′,3′-Dihydroxy-3′-(methoxycarbonyl)propanoyl]bornane-10,2-sultam* ((2′*S*,3′*S*)-**3b**): White solid. M.p. 85–87° (hexane/AcOEt). $[\alpha]_D = -72.3$ (*c* = 1.03, $CHCl_3$). IR: 3492, 3314, 2961, 1750, 1692, 1628, 1459, 1412, 1334, 1291, 1241, 1167, 1137, 1094, 1058, 997, 940, 855, 828, 770, 652. ^{1}H-NMR: 5.09 (*dd*, *J* = 1.8, 8.0, 1 H); 4.78 (*dd*, *J* = 1.8, 6.4, 1 H); 3.97 (*dd*, *J* = 5.7, 6.7, 1 H); 3.87 (*s*, 3 H); 3.59 (*d*, *J* = 8.0, OH); 3.55 (*d*, *J* = 13.8, 1 H); 3.47 (*d*, *J* = 13.8, 1 H); 3.10 (*d*, *J* = 6.4, OH); 2.17–2.03 (*m*, 2 H); 1.89–1.82 (*m*, 3 H); 1.52–1.22 (*m*, 2 H); 1.14 (*s*, 3 H); 0.98 (*s*, 3 H). ^{13}C-NMR: 172.0 (MeO*OC*); 170.6 (C(1′)); 72.8 (C(2′)); 72.4 (C(3′)); 65.0 (C(2)); 53.2 (MeO); 52.9 (C(10)); 49.3 (C(1)); 47.9 (C(7)); 44.3 (C(4)); 37.5 (C(3)); 32.5 (C(6)); 26.5 (C(5)); 20.2 (C(8)); 19.8 (C(9)). EI-MS: 362 ([*M* + H]$^+$), 302 ([*M* − CO_2Me]$^+$). HR-MS: 362.12784 ($C_{13}H_{24}NO_7S^+$, [*M* + H]$^+$; calc. 362.12735).

N,N′-*[(2′*R*,3′*R*)-2′,3′-Dihydroxybutanedioyl]-bis[(2*R*)-bornane-10,2-sultam]* (= *1,1′-[(2*R*,3*R*)-2,3-Dihydroxy-1,4-dioxobutane-1,4-diyl]bis[(3a*S*,6*R*,7a*R*)-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazol] 2,2,2′,2′-Tetraoxide*; (2′*R*,3′*R*)-**2c**): White solid. M.p. 261–263° (hexane/AcOEt). $[\alpha]_D = -108.0$ (*c* = 1.17, $CHCl_3$). IR: 3551, 3461, 2999, 2964, 2905, 1691, 1415, 1329, 1217, 1139, 1068, 991, 760. ^{1}H-NMR: 5.07 (*d*, *J* = 4.2, 2 H); 3.97 (*dd*, *J* = 4.9, 7.8, 2 H); 3.69 (br. *s*, 2 OH); 3.53 (*d*, *J* = 13.8, 2 H); 3.48 (*d*, *J* = 13.8, 2 H); 2.23–2.16 (*m*, 2 H); 2.07 (*dd*, *J* = 7.8, 13.8, 2 H); 1.96–1.85 (*m*, 6 H); 1.45–1.39 (*m*, 2 H); 1.36–1.29 (*m*, 2 H); 1.17 (*s*, 6 H); 0.97 (*s*, 6 H). ^{13}C-NMR: 169.6 (C(1′)); 70.6 (C(2′)); 65.2 (C(2)); 52.8 (C(10)); 49.1 (C(1)); 47.8 (C(7)); 44.7 (C(4)); 38.0 (C(3)); 32.8 (C(6)); 26.3 (C(5)); 20.9 (C(8)); 19.8 (C(9)). LSI-MS: 567 ([*M* + Na]$^+$), 545 ([*M* + H]$^+$). HR-MS: 567.18046 ($C_{24}H_{36}N_2O_8S_2^+$, [*M* + Na]$^+$; calc. 567.18108).

*(2*R*)-*N*-[(2′*R*,3′*S*)-2′,3′-Dihydroxy-3′-phenylpropanoyl]bornane-10,2-sultam* (= *(3a*S*,6*R*,7a*R*)-1-[(2*R*,3*S*)-2,3-Dihydroxy-1-oxo-3-phenylpropyl]-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3*H*-3a,6-methano[2,1]benzisothiazole 2,2-Dioxide*; (2′*R*,3′*S*)-**2d**): White solid. M.p. 205–208° (CCl_4). $[\alpha]_D = -93.2$ (*c* = 1.1, $CHCl_3$). IR: 3600, 3550, 2960, 1673, 1407, 1313, 1221, 1165, 1130, 1084, 1065, 993, 868, 761, 734, 707, 638. ^{1}H-NMR: 7.5–7.25 (*m*, 5 H); 5.25 (*t*, *J* = 4, 1 H); 4.79 (*dd*, *J* = 4, 8, 1 H); 3.94 (*dd*, *J* = 5, 7, 1 H); 3.55 (*d*, *J* = 14, 1 H); 3.47 (*d*, *J* = 8, 1 OH); 3.45 (*d*, *J* = 14, 1 H); 3.02 (*d*, *J* = 4, 1 OH); 2.22 (*m*, 1 H); 2.09 (*dd*, *J* = 8, 13, 1 H); 1.9 (*m*, 3 H); 1.3–1.47 (*m*, 2 H); 1.17 (*s*, 3 H); 0.99 (*s*, 3 H). ^{13}C-NMR: 171.2 (C(1′)); 139.4 (C_{ipso}); 128.4 (2 C_m); 128.0 (C_p); 126.7 (2 C_o); 73.7 (C(3′) or C(2′)); 72.3 (C(2′) or C(3′)); 65.3 (C(2)); 52.9 (C(10)); 49.2 (C(1)); 47.9 (C(7)); 44.6 (C(4)); 38.0 (C(3)); 32.8 (C(6)); 26.4 (C(5)); 20.8 (C(8)); 19.9 (C(9)). MS: 379 (0, $M^{+\cdot}$), 361 (0.2), 273 (12), 152 (40), 135 (65), 119 (20), 105 (68), 91 (50), 77 (100), 67 (30), 51 (40), 41 (65). HR-MS: 379.4739 ($C_{19}H_{25}NO_5S^+$, M$^+$; calc. 379.4742.

(2R)-N-[(2'R,3'S)-2',3'-Dihydroxy-3'-(4-methoxyphenyl)propanoyl]bornane-10,2-sultam (= *(3aS,6R,7aR)-1-[(2R,3S)-2,3-Dihydroxy-3-(4-methoxyphenyl)-1-oxopropyl]-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3H-3a,6-methano[2,1]benzisothiazole 2,2-Dioxide*; (2'*R*,3'*S*)-**2e**): White solid. M.p. 139–141° (toluene). $[\alpha]_D = -94.8$ ($c = 0.64$, $CHCl_3$). IR: 3500, 2970, 1680, 1515, 1245, 1135. ^{1}H-NMR: 7.4 (*d*, *J* = 14, 2 H); 6.89 (*d*, *J* = 14, 2 H); 5.18 (*t*, *J* = 4, 1 H); 4.75 (*dd*, *J* = 4, 8, 1 H); 3.92 (*dd*, *J* = 5, 7, 1 H); 3.79 (*s*, 3 H); 3.53 (*d*, *J* = 14, 1 H); 3.47 (*d*, *J* = 4, 1 OH); 3.46 (*d*, *J* = 14, 1 H); 2.97 (*d*, *J* = 4, 1 OH); 2.22 (*m*, 1 H); 2.08 (*dd*, *J* = 8, 13, 1 H); 1.9 (*m*, 3 H); 1.3–1.47 (*m*, 2 H); 1.16 (*s*, 3 H); 0.98 (*s*, 3 H). ^{13}C-NMR: 171.0 (C(1')); 159.3 (C_p); 131.4 (C_{ipso}); 128.0 (2 C_o); 113.8 (2 C_m); 73.7 (C(3')); 71.9 (C(2')); 65.2 (C(2)); 55.2 (MeO); 52.8 (C(10)); 49.2 (C(1)); 47.9 (C(7)); 44.5 (C(4)); 38.0 (C(3)); 32.8 (C(6)); 26.4 (C(5)); 20.8 (C(8)); 19.8 (C(9)). MS. 409 (0.2, $M^{+\cdot}$), 273 (20), 152 (21), 135 (100), 107 (20), 77 (23), 43 (14).

(2R)-N-[(2'R,3'S)-2',3'-Dihydroxy-3'-(4-nitrophenyl)propanoyl]bornane-10,2-sultam (= *(3aS,6R7aR)-1-[(2R,3S)-2,3-Dihydroxy-3-(4-nitrophenyl)-1-oxopropyl]-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3H-3a,6-methano[2,1]benzisothiazole 2,2-Dioxide*; (2'*R*,3'*S*)-**2f**): White solid. M.p. 186–188° (EtOH). $[\alpha]_D = -96.9$ ($c = 0.8$, $CHCl_3$). IR: 3480, 2960, 1665, 1520, 1345, 1135. ^{1}H-NMR: 8.21 (*d*, *J* = 8, 2 H); 7.66 (*d*, *J* = 8, 2 H); 5.36 (*d*, *J* = 4, 1 H); 4.78 (*d*, *J* = 4, 1 H); 3.93 (*dd*, *J* = 5, 7, 1 H); 3.57 (*d*, *J* = 14, 1 H); 3.53 (*s*, 1 OH); 3.49 (*d*, *J* = 14, 1 H); 2.22 (*m*, 1 H); 2.09 (*dd*, *J* = 8, 14, 1 H); 2.04 (*s*, 1 OH); 1.9 (*m*, 3 H); 1.3–1.49 (*m*, 2 H); 1.15 (*s*, 3 H); 0.99 (*s*, 3 H). ^{13}C-NMR: 170.8 (C(1')); 147.6 (C_p); 146.8 (C_{ipso}); 127.7 (2 C_o); 123.5 (2 C_m); 73.3 (C(3')); 71.6 (C(2')); 65.3 (C(2)); 52.8 (C(10)); 49.4 (C(1)); 47.9 (C(7)); 44.5 (C(4)); 37.9 (C(3)); 32.8 (C(6)); 26.4 (C(5)); 20.7 (C(8)); 19.8 (C(9)). MS: 424 (0, $M^{+\cdot}$), 407 (1), 295 (4), 273 (11), 221 (10), 178 (9), 150 (79), 135 (94), 108 (41), 93 (72), 67 (46), 55 (54), 43 (100).

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