

# The First Entry to Complex Bakkanes: A Highly Effective Retroaldol–Aldol-Based Approach to (–)-Bakkenolides III, B, C, and H\*\*

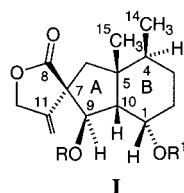
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*Dedicated to Prof. Jean Lhomme  
on the occasion of his retirement*

Since the first members were isolated and elucidated in the late 1960s, the bakkanes have rapidly increased in number, particularly recently, so as to count now approximately 50.<sup>[1]</sup> These hydrindane sesquiterpenes of both terrestrial and marine origin, characterized by their novel spiro  $\gamma$ -butyrolactone function and significant biological effects,<sup>[1m,n,2]</sup> have become popular synthetic targets. To date bakkenolide A, homogynolides A and B, palmosalide C, and 9-acetoxylukinanolide have been prepared, most more than once.<sup>[3]</sup>

The nonfunctionalized and monofunctionalized bakkenolides, however, are each oxygenated singly and taken together comprise only a relatively minor number of the known bakkanes. Much more representative (ca. 80 %) of this class are the densely functionalized and stereochemically challenging C1,C9-dioxygenated bakkenolides (**1**, **R**, **R**<sup>1</sup> = H, acyl). These compounds, which have significant inhibitory activity toward Hep G2, Hep G2.2,15, and P-388 tumor cell lines,<sup>[1n]</sup> as well as PAF, arachidonic acid, and collagen-induced platelet aggregation,<sup>[1m]</sup> have been isolated from *Petasites japonicus* Maxim. and *Petasites formosanus* Kitamura (Compositae).<sup>[1b–f, m, n]</sup>

Herein we illustrate the first entry to this large group of bakkanes through the preparation of the representative natural bakkenolides III, B, C, and H (**1–4**). We note in



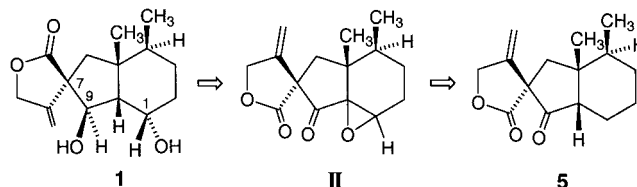
- 1**, **R** = **R**<sup>1</sup> = H Bakkenolide III  
**2**, **R** = H; **R**<sup>1</sup> = COC(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>3</sub>) Bakkenolide C  
**3**, **R** = COCH<sub>3</sub>; **R**<sup>1</sup> = COC(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>3</sub>) Bakkenolide B  
**4**, **R** = **R**<sup>1</sup> = COCH(CH<sub>3</sub>)<sub>2</sub> Bakkenolide H

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[\*\*] We thank Dr. A. Durif, Dr. M.-T. Averbuch, and Dr. C. Philouze for the X-ray structure determinations, Ms. M.-L. Dheu-Andries for help with the molecular modeling studies, Mr. F. Bargiggia and Mr. M. Cook for some preliminary experiments, and Prof. M. Kawai (Nagoya Institute of Technology) for samples of natural bakkenolide B and bakkenolide III. Financial support from the Université Joseph Fourier and the CNRS (UMR 5616), as well as a fellowship award from the MESR to O.H. are gratefully acknowledged.

advance that this highly stereocontrolled and efficient approach allows potentially total access to the group.

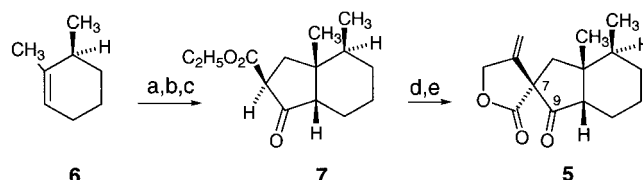
With its six stereocenters in the proper configurations and two hydroxyl groups which could be, in principle, easily differentiated, diol **1** (bakkenolide III) appeared to be the ideal late intermediate for accessing the entire range of known C1,C9-difunctionalized bakkenolides (Scheme 1). It seemed this diol might be secured from epoxy ketone **II** through chemoselective reduction, followed by stereochemical adjustments.



Scheme 1. Retrosynthesis of bakkenolide III (**1**).

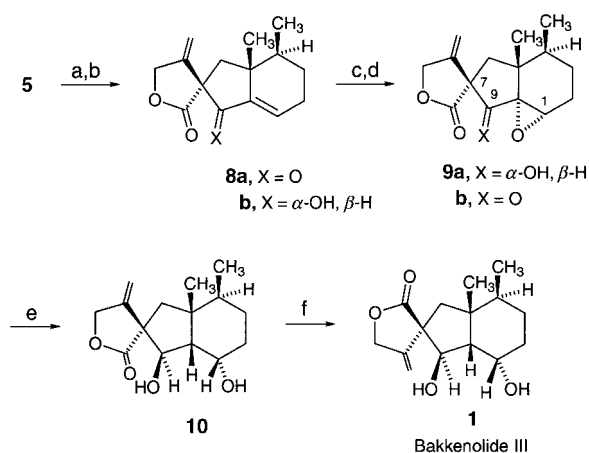
Molecular mechanics calculations<sup>[4]</sup> revealed diol **1** to have the lowest global minimum energy of the four C7,C9 diastereomers, thus it could possibly be reached through a retroaldol–aldol equilibration. Epoxy ketone **II**, in turn, was viewed as arising from keto lactone **5**, an intermediate previously prepared in our laboratory from 1,6-dimethylcyclohexene.<sup>[3n,5]</sup>

Keto lactone **5** was synthesized stereoselectively from enantiopure 1,6-dimethylcyclohexene (**6**)<sup>[3d]</sup> in five steps and 27 % overall yield<sup>[6]</sup> in a manner similar to that used earlier. It was found, however, that ring expansion could be improved by using boron trifluoride as the catalyst and that neutral conditions benefitted the transesterification<sup>[7]</sup> (Scheme 2).



Scheme 2. Synthesis of keto lactone **5**. a) Ref. [3d, n]; b) Zn, CH<sub>3</sub>CO<sub>2</sub>H, 70 °C, 1 h (63 %, 2 steps); c) N<sub>2</sub>CHCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, 0 °C, 12 h (72 %); d) HC≡CCH<sub>2</sub>OH, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, reflux, 24 h (87 %); e) Mn(O<sub>2</sub>CCH<sub>3</sub>)<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, 20 °C, 2.5 h (68 %).

Of the numerous procedures examined for effecting dehydrogenation of this keto lactone to its  $\Delta^{1(10)}$  derivative **8a**, phenylselenenylation/oxidation<sup>[8]</sup> was clearly the most efficacious and under carefully optimized conditions the sensitive enone could be isolated in 77 % yield (Scheme 3). Base-catalyzed epoxidations with this derivative invariably resulted in degradation, and so a hydroxyl-directed procedure was next considered. Toward this end, enone **8a** was subjected to a Luche reduction in ethanol,<sup>[9]</sup> which led cleanly and highly stereoselectively ( $\geq 98:2$ ) to the retroaldol-prone allylic alcohol **8b**, in which the hydroxyl group had the desired  $\alpha$  orientation.<sup>[10]</sup> This material was exposed without purification to a [VO(acac)<sub>2</sub>]-catalyzed epoxidation with *tert*-butyl hydroperoxide (TBHP) in warm toluene<sup>[11]</sup> to provide selectively the required epoxide **9a**, which was isolated in 57 %



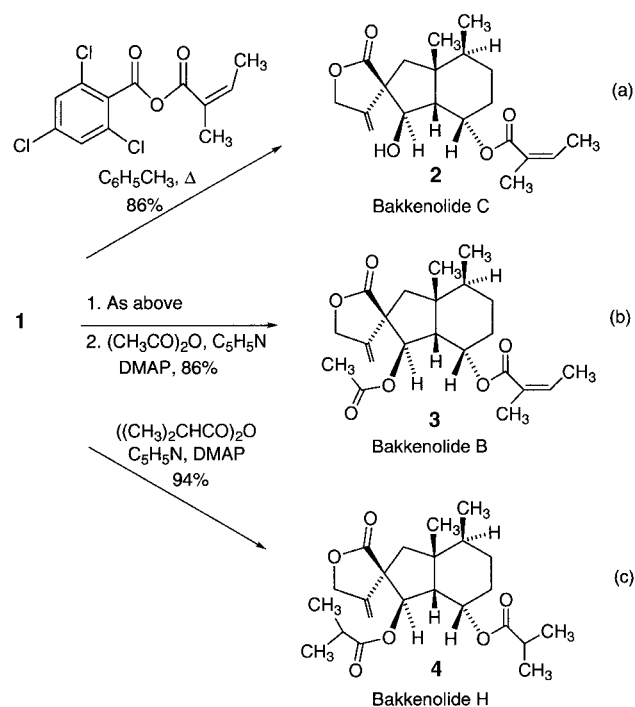
Scheme 3. Synthesis of bakkenolide III (**1**). a) NaHMDS, THF,  $-65^{\circ}\text{C}$ , 4 h;  $\text{C}_6\text{H}_5\text{SeBr}$ ,  $-65 \rightarrow 0^{\circ}\text{C}$ , 1 h;  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{CO}_2\text{H}/\text{H}_2\text{O}$ ,  $0^{\circ}\text{C}$ , 1.5 h (77 %); b)  $\text{NaBH}_4$ ,  $\text{CeCl}_3$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $-30^{\circ}\text{C}$ , 1.5 h; c)  $[\text{VO}(\text{acac})_2]$ , TBHP,  $\text{C}_6\text{H}_5\text{CH}_3$ ,  $50-60^{\circ}\text{C}$ , 6 h (57 %, 2 steps); d)  $(\text{ClCO})_2$ , DMSO,  $\text{CH}_2\text{Cl}_2$ ,  $-60^{\circ}\text{C}$ , 15 min;  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $-60 \rightarrow 20^{\circ}\text{C}$ , 1 h (83 %); e)  $\text{SmI}_2$ , THF/ $\text{H}_2\text{O}$ ,  $20^{\circ}\text{C}$ , 0.5 h (83 %); f)  $(\text{C}_4\text{H}_9)_4\text{NF}$ , THF,  $0^{\circ}\text{C}$ , 0.5 h (82 %). acac = acetylacetonate; DMSO = dimethyl sulfoxide; HMDS = 1,1,1,3,3,3-hexamethyldisilazide; TBHP = *tert*-butyl hydroperoxide.

yield (2 steps). Swern oxidation then gave efficiently epoxy ketone **9b** and set the stage for reduction to the C1,C9-diol.

Previous experience had shown  $\text{SmI}_2$  to be uniquely effective for the reduction of 7-*epi*-9-oxo-bakkenolide A (**5**).<sup>[3n]</sup> It was therefore hoped that this reagent, also known to be able to effect reductive cleavage of  $\alpha$  heteroatom substituents in ketone derivatives, used in excess and in a protic medium might produce a chemoselective double reduction of epoxy ketone **9b**.<sup>[12]</sup> A clean transformation, in fact, resulted when excess reagent in 1 % aqueous THF was used at room temperature for 0.5 h and delivered only the C1 $\alpha$ ,C9 $\beta$ -diol derivative **10** in 83 % yield. A single-crystal X-ray analysis corroborated these assignments.<sup>[13]</sup>

The success of the entire venture now hinged on the thermodynamics predicted by molecular modeling studies<sup>[4]</sup> for the retroaldol–aldol transformation of lactone diol **10**.<sup>[14]</sup> To our considerable satisfaction, **10** underwent smooth isomerization, in spite of numerous possible alternative pathways, on exposure to tetrabutylammonium fluoride (TBAF) in THF at  $0^{\circ}\text{C}$  for 0.5 h to provide a single, crystalline lactone diol in high yield. Confirmation that the crucial conversion had in fact occurred as predicted to deliver the key compound, (–)-bakkenolide III (**1**),<sup>[1n]</sup> was obtained by direct comparison with the hydrolysis product<sup>[1b,d,f]</sup> of (–)-bakkenolide B and through single-crystal X-ray analysis.<sup>[15]</sup>

The hydroxyl groups in bakkenolide III are clearly in different steric environments and this was expected to translate into regioselective acylations. Bakkenolide III in the presence of the Yamaguchi mixed anhydride derived from angelic acid and under conditions earlier found to avoid the facile angelic  $\rightarrow$  tiglic isomerization<sup>[16]</sup> formed (–)-bakkenolide C (**2**)<sup>[1d]</sup> in 86 % yield without detectable amounts of C9-acylated material or tiglic ester (Scheme 4a). The bakkenolide C so obtained was identical with a sample secured by partial hydrolysis<sup>[1b,d,f]</sup> of natural bakkenolide B.



Scheme 4. Synthesis of a) bakkenolide C (**2**), b) bakkenolide B (**3**), and c) bakkenolide H (**4**). DMAP = 4-dimethylaminopyridine.

In the presence of excess anhydride and 4-dimethylaminopyridine (DMAP), however, C9 acylation could be readily achieved. Thus, (–)-bakkenolide B (**3**)<sup>[1b,d,f,n]</sup> could be secured in 86 % yield from (–)-bakkenolide C with excess acetic anhydride in pyridine in the presence of DMAP (Scheme 4b). Likewise, (–)-bakkenolide H (**4**)<sup>[1m,n]</sup> which shows significant cytotoxic activity in several test systems, could be prepared in 94 % yield from bakkenolide III by using excess isobutyric anhydride under similar conditions (Scheme 4c).

In summary, enantiopure (–)-bakkenolide III has been efficiently synthesized (>6 % overall yield, 11 steps) through a highly stereocontrolled approach and used as a platform for accessing representative C1,C9-dioxygenated bakkenolides. This first successful entry to these numerous bioactive compounds relies on a novel  $\text{SmI}_2$ -promoted chemoselective double reduction of an epoxy ketone to generate the C1 and C9 hydroxyl groups and a thermodynamically governed retroaldol–aldol strategy to install the spiro lactone unit and the C9 hydroxyl group with the proper stereochemistry. Both of these should find additional application.

Received: July 21, 2000 [Z 15504]

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- [13] Crystal data for ( $\pm$ )-**10** (from parallel studies):<sup>[17]</sup> C<sub>15</sub>H<sub>22</sub>O<sub>4</sub>, tetragonal, *I*<sub>4</sub>/a, *a* = 20.220(7), *c* = 13.427(7) Å, *V* = 5490(3) Å<sup>3</sup>, *Z* = 16,  $\rho_{\text{calcd}} = 1.289$  Mg m<sup>-3</sup>, *F*(000) = 2304,  $\theta = 2.0$ – $30^\circ$ , 5466 measured reflections, 5274 (*R*(int) = 0.017) independent reflections, *R*(*F*) (*F* > 2 $\sigma$ (*F*)) = 0.0487, *wR* (all data) = 0.0512, GOF = 1.965.
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## A Tandem Sulfur Transfer/Reduction/Michael Addition Mediated by Benzyltriethylammonium Tetrathiomolybdate\*\*

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Disulfides and sulfur containing organic compounds are important functional groups widely present in nature and have commercial significance.<sup>[1]</sup> Therefore, the synthesis of disulfides, sulfides, and  $\omega$ -thio ketones is not only attractive but also finds numerous applications.<sup>[2]</sup> Studies directed

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[\*\*] This work was supported by the Department of Science and Technology, New Delhi.