

## Natural Product Letters

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gnpl19>

## Biomimetic Synthesis and Absolute Configuration of (-)-Tanzanene

Sashikumar K. Paknikar<sup>a</sup>, Kamalesh Pai Fondekar<sup>a</sup> & Ralf Mayer<sup>b</sup>

<sup>a</sup> Department of Chemistry, Goa University, Talegaon Plateau, Goa, 403 203, India

<sup>b</sup> Pharmazeutisches Institut, Universität Bonn, Kreuzbergweg 26, D-53115, Bonn, Germany

Published online: 04 Oct 2006.

To cite this article: Sashikumar K. Paknikar, Kamalesh Pai Fondekar & Ralf Mayer (1996) Biomimetic Synthesis and Absolute Configuration of (-)-Tanzanene, *Natural Product Letters*, 8:4, 253-256, DOI: [10.1080/10575639608044903](https://doi.org/10.1080/10575639608044903)

To link to this article: <http://dx.doi.org/10.1080/10575639608044903>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## BIOMIMETIC SYNTHESIS AND ABSOLUTE CONFIGURATION OF (-)-TANZANENE

SHASHIKUMAR K. PAKNIKAR<sup>\*a</sup>, KAMALESH PAI FONDEKAR<sup>a</sup>  
and RALF MAYER<sup>b</sup>

a) Department of Chemistry, Goa University, Talegaon Plateau, Goa 403 203, India

b) Pharmazeutisches Institut, Universität Bonn, Kreuzbergweg 26, D-53115 Bonn, Germany

(Received 9 April 1996)

**Abstract:** Biomimetic synthesis of (-)-tanzanene (1) from (-)-alloaromadendrene (4) is reported. This first synthesis of (-)-tanzanene also established its absolute configuration as shown in 1.

**Key Words:** (-)-tanzanene, [4+2]cycloaddition, (-)-alloaromadendrene, 6-methylene-2,4-cyclohexadiene-1-one, o-quinone methide, hetero Diels-Alder reaction, *Uvaria*.

### INTRODUCTION

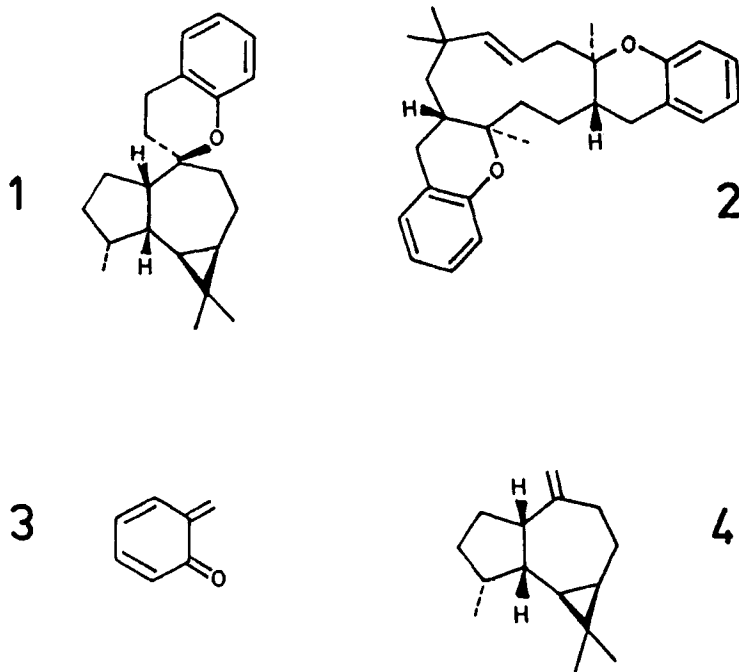
The genus *Uvaria* has been a source of several new bioactive compounds which are C-benzylated flavanoids, chalcones, dihydrochalcones and other aromatic skeletons. Novel meroterpenoids such as tanzanene (1) and lucidene (2) have been isolated from *Uvaria tanzaniae* Verdc.<sup>1</sup> and *U. lucida* ssp. *lucida*<sup>2</sup> respectively.

### RESULTS AND DISCUSSION

Derivation of the stereostructure 1 for tanzanene by a detailed spectroscopic analysis gives hints to a possible biosynthesis by a hetero[4+2]cycloaddition of

o-quinone methide (3) to the exocyclic double bond of alloaromadendrene (4) resulting in the novel spirobicyclo structure 1. While the structures of 1 and 2 are established unambiguously, there is no report on their synthesis. Moreover, natural tanzanene (1) is laevorotatory and its absolute configuration is not known.

In connection with our work on the chemical constituents of *Uvaria narum* and our continued interest in the synthesis of terpenoids, we initiated a study to generate the o-quinone methide (3) from o-hydroxybenzyl alcohol (saligenin) in the presence of unsaturated substrates including mono- and sesquiterpene hydrocarbons. In this communication, we wish to report a simple biomimetic synthesis of (-)-tanzanene (1) from (-)-alloaromadendrene (4), a sesquiterpene of known absolute configuration<sup>3</sup> which may support the proposed [4+2]cycloaddition and which also establishes the absolute configuration of (-)-tanzanene as shown in 1.



o-Quinone methide (3) has been generated from o-hydroxybenzyl alcohol, or o-hydroxybenzyl halides and o-cresol and used in hetero Diels-Alder reactions<sup>4</sup>. Thermal reaction of saligenin and styrene is reported to yield 2-phenylchroman, obviously via the in situ generated o-quinone methide (3) and the olefinic linkage of styrene<sup>5</sup>. We have found that 3 can be generated by refluxing a solution of saligenin in dry xylene and readily adds to various olefinic linkages to produce [4+2]cycloaddition products<sup>6</sup>.

Refluxing an equimolar mixture of saligenin and (-)-alloaromadendrene (4) in dry xylene for 12 hr, followed by chromatography over silica gel resulted in the recovery of unchanged 4 and isolation of a crystalline compound, m. p. 84°C (lit.<sup>1</sup> 84-85°C),  $[\alpha]_D^{25} = -7.1^\circ$  (c=0.18, CHCl<sub>3</sub>), overall yield : 21%.

A direct comparison of the IR, UV, <sup>1</sup>H, <sup>13</sup>CNMR spectra of the synthetic compound and those reported of natural tanzanene (1), co-TLC and mixture m. p. determination unambiguously established their identity. In addition, the sign and magnitude of specific rotation of the synthetic tanzanene established the absolute configuration of natural (-)-tanzanene as shown in 1.

#### ACKNOWLEDGEMENTS

The authors thank Prof. Dr. H. Achenbach for copies of the IR, UV, <sup>1</sup>H, <sup>13</sup>CNMR, mass spectra and authentic natural (-)-tanzanene. We are grateful to M/s Fluka Chemie AG for a precious gift of (-)-alloaromadendrene and Govt. of Goa and CSIR, New Delhi, (SRF to KPF) for financial support.

**REFERENCES AND NOTES**

1. H. Weenen, M. H. H. Nkunya, Q. A. Mgani, M. A. Posthumus, R. Waibel and H. Achenbach (1991) Tanzanene, Spiro-Benzopyranyl Sesquiterpene from *Uvaria tanzaniae* Verdc.. *Journal of Organic Chemistry*, **56**, 5865 - 5867.
2. H. Weenen, M. H. H. Nkunya, A. A. El Fadl, S. Harkema and B. Zwanenburg (1990) Lucidene, Bis(benzopyranyl) Sesquiterpene from *Uvaria lucida* ssp. *lucida*. *Journal of Organic Chemistry*, **55**, 5107 - 5109, and references cited therein.
3. G. Büchi, W. Hofheinz and J. V. Paukstelis, (1969), The Synthesis of (-)-Aromadendrene and Related Sesquiterpenes. *Journal of the American Chemical Society*, **91**, 6473 - 6478, and references cited therein.
4. A. B. Turner (1964) Quinone Methides. *Quarterly Reviews*, The Chemical Society London, **18**, 347 - 360.
5. K. Hultzsch (1941) Die Reaktion von Phenylalkoholen mit ungesättigten Substanzen. *Journal für Praktische Chemie*, **158**, 275 - 294; *Chemical Abstracts*, (1942), **36**, 849.
6. Details and further applications will be published elsewhere.