We are IntechOpen, the world’s leading publisher of Open Access books. Built by scientists, for scientists.

4,300 Open access books available
116,000 International authors and editors
130M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com
Abstract

Recent developments in selected sesquiterpenoids are reviewed for the past one decade (2005–2017) with special reference to Mechanisms of multistep molecular rearrangements of some sesquiterpenes or derivatives based on isotopic labeling studies and extensive spectroscopic analysis such as molecular rearrangement of acetyl cedrene to cedrene follower, acid catalyzed rearrangement of morelaine-based triketone, synthesis of (R)-isocomene and (R)-triquinane by acid-catalyzed rearrangement of (R)-modhephene, Total synthesis of (R)-cymbiodiacetal, BF$_3$ catalyzed molecular rearrangements of mono epoxides of α- and β-himachalenes, santonic acid: Zn-HCl-ether reduction. Insights into biosynthesis of albaflavenone, caryol-1(11)-ene-10-ol, (R)-koraial, pogostol, patchouli alcohol and valerenadiene are discussed. Congeners for probing structure-biosynthetic relationship. This approach is discussed with the availability of very interesting results on the isolation of highly oxygenated secondary metabolites from endophytic fungi, Xylaria sp.

Keywords: molecular rearrangements, mechanisms, synthetic application, CCR, biosynthesis, labeling experiments, congeners

1. Introduction

Sesquiterpene carbon frameworks comprise the largest group of terpenoids or sometime referred as isoprenoids. Farnesyl diphosphate (FPP) having three olefinic linkages undergo cyclization to produce very large number major cyclic frameworks which are further modified by oxidative cleavages, molecular rearrangements, loss of carbon atoms. The aim of this chapter is to provide an overview of the recent developments in sesquiterpenes with
particular reference to molecular rearrangements, biosynthesis and structural relationship among congeners. The coverage is not comprehensive but a focused review of the literature (2005–till September 2017) and only the relevant research articles having a link with the above areas are selected for discussion.

2. Mechanisms of multistep molecular rearrangements, insight into biosynthesis and congeners for probing structure-biosynthetic relationship of selected natural products

2.1. Molecular rearrangement of acetyl cedrene to cedrene follower

The acetylation of cedrene 1 can lead to various products depending on the reaction conditions. Paknikar et al. [1] undertook a detailed study on the acetylation of cedar wood oil (Virginia) with acetic anhydride and polyphosphoric acid in dichloromethane which leads, besides acetyl cedrene 2, also to a minor product, 1,7,7-trimethyl-2,3-(3′4′-dimethylbenzo) bicyclo[3.2.1]-octane 3, called the follower. Structural analysis of 3 (Scheme 1) shows that rings A, B, C of 2 are rearranged as B, A, C in follower 3.

Formation of 3 from 2 can only be explained by a multistep intramolecular rearrangement. This shows that: (i) ring C of 2 has undergone initial ring enlargement and subsequent ring contraction; (ii) cleavage of the C6–C7 bond of 2 and formation of the new C6-C2 bond; (iii) enlargement of ring A of 2 with concomitant loss of water. The mechanism for the formation of 3 from 2 when 1-13C labeled acetic anhydride was used is shown in Scheme 2.
One characteristic feature of the formation of the follower 3 is sluggish reaction rates. Density Functional Theory (DFT) calculation of B3LYP/6-31G* type using the Gaussian version 09 (Gaussian) revealed that the first neutral intermediate 4 (Scheme 2) is higher in energy than acetyl cedrene by ~20 kcal. A series of further cascade-like cationic rearrangements is involved with breaking and bond-forming intermediates.

The formation of the neutral intermediate 4 is supported by the observation that this process is the reverse pathway for the biosynthesis of α-cedrene from FPP, which has been established previously [2]. Few other feasible mechanisms for the formation of follower 3 could be devised, and only the one presented fits the observation of 13C enriched label at the C-3′ position of follower 3. Hence the key rearrangement is cyclopropylcarbinyl cation-cyclopropylcarbinyl cation rearrangement (CCR) [3, 4]. During the deuteriation of commercial acetyl cedrene, the follower was also deuterated, and it was observed that aromatic protons are exchanged. Interestingly, the product was only monodeuterated (Scheme 1) and the isotope was shared equally between the C-5′ and C-6′ positions of the follower 3. This equal distribution of one deuterium atom between C-5′ and C-6′ can be accounted for by the facile 1,2-hydride and 1,2-deuteride shifts and equilibration.

2.2. Acid catalyzed rearrangement of morelaine based triketone. Characterization of keto lactone, a 1–11 seco-morelaine

An interesting molecular rearrangement has been reported by Morales and co-workers [5]. They observed that triketone 5 on treatment with p-TSA in benzene resulted in the formation of a keto lactone 6, a 1–11 seco-morelaine derivative and also the first representative of this group (Figure 1).

The rearrangement depicted in Scheme 3 involves initial cyclobutane ring expansion of the protonated triketone, generation of carbocationic intermediate 7 which rearranges via transition state in to protonated seco-morelaine 8. These steps are supported by DFT calculations.
Triquinanes have received considerable attention by their unique structure as well as their reported biological activities. (−)-Modhephene of established absolute stereochemistry was subjected to acid catalyzed carbocation rearrangements which led to an interesting synthesis of (−)-isocomene and (−)-triquinane [6]. This study was extended further by preparation of (−)-modhephene stereospecifically at 14β geminal methyl group. Under same experimental conditions, deuterium labeled (−)-triquinane a stereospecific 1,2-migration of 7/4β methyl group was observed (Scheme 4).

2.4. Total synthesis of (+)-cymbodiactetal

In 2010, Hayes and his co-workers reported [7] a total synthesis of (+)-Cymbodiacetal by a biomimetic route proposed earlier [8, 9] using (R)-(−)-limonene, the key step involves hetero Diels-Alder cycloaddition which proceeds with an endo selectivity (2:1) in a quantitative
Exploitation of exo-isomer with m-CPBA followed by acid catalyzed opening afforded (+)-cymbodialcolal 12 (Scheme 5). The uncertainty in absolute stereochemistry was independently established by X-ray crystallography. These studies also clarified discrepancies in the previously published work [8, 9].
2.5. BF₃ catalyzed molecular rearrangements of mono epoxides of α- and β-himachalenes

Previous examples of acid catalyzed rearrangements of sesquiterpenes have shown that the opening of the epoxide triggers the reaction and directs the subsequent molecular rearrangements. In practically, among all the cases the aim is to valorize the naturally occurring sesquiterpene hydrocarbons.

Manoury and co-workers [10] observed that on treatment of α-himachalene monoepoxide 14 with BF₃-Et₂O in CH₂Cl₂ at room temperature afforded a tricyclic ketone 16 (71% isolated yield) product along with an unsaturated alcohol 17 (18%). The structure 16 was unambiguously assigned to ketone based on ¹H, ¹³C, ¹H-2D NMR experiments. The proposed mechanism (Scheme 6) involves ring opening of epoxide followed by participation of terminal methylene group to generate a tricyclic bridgehead carbocation 18 by ring contraction of seven membered ring to generate intermediate 19. A stereospecific 1,4-hydride transfer is proposed in the last step to the formation of 16.

Inspection of molecular models of intermediate 19 shows that the proposed stereospecific 1,4-hydride shift is unlikely and therefore a different process is responsible for the formation of ketone 16.

The structure assignment 17 to the minor product, a tricyclic unsaturated alcohol is based on spectral analysis and confirmed by single crystal X-ray data. The characteristic feature of 17 is the presence of a double bond involving a bridgehead carbon.

β-Himachalene monoepoxide 15 under identical experimental conditions gave two products major product (62%) and aryl-himachalene (10%). The major product was assigned structure 20. The proposed mechanism explains formation of 20 (Scheme 7). The gross structure of this compound an allo-himachalol, a natural product isolated from Cedrus deodara [11].
Compounds 16, 17 and 20 are all optically active and since the absolute stereochemistry of himachalenes are known, it is observed that C7 α-H of α-himachalenes remains intact throughout the rearrangement. The absolute stereochemistry of 16, 17 and 20 is shown in Figure 2.

2.6. Santonic acid: Zn-HCl-ether reduction

Santonic acid 21 (the diketocarboxylic acid obtained from santonin on digestion with aq. alkali) was subjected to reduction with the Zn-HCl-ether system [12] with an aim to obtain the previously prepared pinacol 22 via intramolecular pinacolisation primarily because of conformational structure of santonic acid with close proximity of the 1,4-diketone system. Under these conditions santonic acid 21 did not afford the pinacol 22, but yielded a 60:40 mixture (GCMS, 1H NMR) of succinic anhydride derivatives 23 and 24. It is clear that the reaction proceeds via pinacol 22, which, under strong acidic conditions, undergoes further rearrangement to give anhydrides 23 and 24 (Scheme 8).


Figure 2. Absolute stereochemistries of ketone 16 alcohol 17 and ketone 20.
2.7. Biosynthesis of albaflavenone

The tricyclic sesquiterpene antibiotic albaflavenone 25 isolated from the gram positive soil bacteria *Streptomyces coelicolor* A3 and *Streptomyces albidoflavus* is biosynthesized by enzymes encoded in a two-gene operm [13]. Initially, the sesquiterpene epi-isozizaene synthase catalyzes the cyclization of 2E, 6E-farnesyl diphosphate (FPP) to (+)-epi-isozizaene 26. A two-step allylic oxidation of 26 catalyzed by a single cytochrome P450170A1 (crP170A1) results in the formation of (+)-albaflavenone 25 via an epimeric mixture of (5S)-albaflavenol 27 and (5R)-albaflavenol 28 intermediates (Scheme 9) [14].

The mechanism and stereochemistry of FPP to epi-isozizaene 26 via (3R)-nerolidyl diphosphate 29 has been conclusively established by labeling studies [15]. The entire biosynthetic process from FPP to epi-isozizaene is shown (Scheme 10). A two-step chemical synthesis of albaflavenone 25 from epi-isozizaene 26 was reported in this study.
Ito and co-workers [16] reported a concise nine step total synthesis of albaflavenone without use of any protecting groups. Moreover, the absolute configuration of naturally occurring (+)-albaflavenone has been unambiguously established as $1S$, $7S$ and $8R$.

2.8. The biosynthesis of caryol-1(11)-ene-10-ol: on the mechanism of the formation of caryolene: a putative biosynthetic precursor to caryol-1(11)-ene-10-ol

In 2013, Nguyen and Tantillo [17] investigated the mechanism of the formation of caryolene 30, a putative biosynthetic precursor to caryol-1(11)-ene-10-ol 31 by DFT calculations (Figure 3).

Quantum chemical calculations indicated the mechanism involving a secondary carbocation intermediate 32 is not energetically viable. They proposed two mechanisms for caryolene 30 formation (pathway a and b). The pathway involves a base catalyzed deprotonation/reprotonation sequence and a tertiary carbocation minima (more likely) whereas...
pathway b involves intramolecular proton transfer and the generation of a secondary carboxylation minima. Both mechanisms are predicted to involve concerted suprafacial/suprafacial [2 + 2] cycloaddition, whose asynchonicity allows them to avoid the constrains of orbital symmetry (Scheme 11).

Scheme 11. Proposed mechanisms for the formation of 1,10-caryolene 30.

2.9. Biosynthesis of (+)-koraiol

As an outcome of Tantillo’s mechanism for caryolene 30 [17], biosynthetic pathway for koraiol 31 becomes evident (Scheme 12).
9-epi-E-Caryophyllene 32, caryophyllene 33 and (+)-koraio 31 were identified by Dickschat and co-workers [18, 19] who carried out investigation on the volatiles of *Fusarium fujikuroi* by the use of CLSA-GCMS. The sesquiterpenoids were divided in to two groups based on their proposed biosynthetic pathways. Volatile sesquiterpenoids produced by sesquiterpene cyclase Ffsc4 were characterized as β-caryophyllene and an optically active alcohol (+)-koraiol 31. The structure 31 was assigned by extensive spectral analysis. The relative configuration of (+)-koraiol was elucidated by NOESY experiments. The cis fusion of rings A and B was deduced from the NOESY couplings of the bridge head hydrogen atoms 1H and 9H with each other with methyl protons 15-H and the pro-5-methylene protons 3-H. Interestingly, Khan et al. isolated (+)-koraiol, [α]_D + 31.7° from the oleoresin of Korean pine (*Pinus koraiensis* Sieb.). The relative stereochemistry as shown in 31 has been established by X-ray analysis [20]. The absolute stereostructure of the rare sesquiterpene (+)-9-epi-E-caryophyllene, an enantiomer of 32 was isolated from *Dacrydium cupressinum* by Weavers and co-workers [21] (Figure 4).

It is tempting to speculate (+)-koraiol 31 is biosynthesized from 9-epi-E-caryophyllene 32.

![Scheme 12. Biosynthesis of (+)-koraiol 31.](image)

![Figure 4. Structures of 9-epi-E-Caryophyllene 32, caryophyllene 33 and (+)-koraiol 31.](image)
2.10. Biosynthesis of Pogostol

Biosynthesis of pogostol 34 by the endophytic fungus *Geniculosporium* was investigated by Dickschat and co-workers [22]. In this study, six 13C labeled isotopomers of mevalonolactone were synthesized and used in feeding experiments with the endophytic fungus *Geniarlosperium*. Feeding experiments with 35a and 35b gave insights into the stereochemical course of the terpene cyclization. The methyl group of the mevalonolactone that is labeled in these two isotopomers is converted into terminal (z)-methyl group of FPP (C-13). Both feeding experiments showed that the deprotonation step leading to germacrene A 36 proceeds with stereospecific deprotonation of C-13 and not C-12 of FPP (Figure 5).

![Figure 5. Biosynthesis of Pogostol 34 using isotopomers of mevalonolactone.](image)

The volatile fraction was extracted by closed loop stripping apparatus followed by direct 13CNMR analysis (CLSA-NMR) newly developed by the same group. The biosynthesis of pogostol 34 proceeds through initial formation of germacrene-A 36. Protonation of 4,5 double bond initiates a second cyclization to cation which gets neutralized with water to give pogostol 34 (Scheme 13).

In view of correlation of (−)-pogostol 37 with (+)-bulnesol 38 with known absolute stereochemistry, (−)-pogostol be represented by the stereostructure 37 [23–25]. The stereostructure 34 thus represents (+)-pogostol (Figure 6).

2.11. Biosynthesis of patchouli alcohol (patchoulol)

The history of patchouli alcohol 39 from its isolation till date has narrated in a recent exhaustive review article [26]. Biosynthetic pathways were proposed based on experimental work for the conversion of FPP to patchouli alcohol 39 (Scheme 14).
Scheme 13. Mechanism of pogostol 34 formation from FPP.

Figure 6. Absolute stereochemistry of (−)-pogostol 37—correlation of (−)-pogostol 37 and (+)-bulnesol 38.

Scheme 14. Mechanism proposed for cyclization and rearrangement of FPP to patchoulol 39.
Croteau et al. [27] and Akhila et al. [28] proposed biosynthetic pathways for the conversion of FPP to patchouli alcohol 39 based on experimental work. Croteau et al. reported the 1,3-shift for conversion of 40 to 41 while Akhila et al. proposed two consecutive 1,2-hydride shifts for the same conversion (Scheme 15).

The recent isotopic labeling studies of Coates and colleagues [29] unrevealed the biosynthetic pathways for 39 which confirmed the 1,3-hydride shift across the five membered ring ruling out two consecutive 1,2-hydride shifts (Scheme 16).
Incubation of isotopically pure [2-2H2] (E,E)-farnesylsulfate with recombinant patchoulol synthase (rPTS) from *Pogostemon cablin* afforded a 65:35 mixture of monodeuterated and di-deuterated patchoulols and several hydrocarbons of which eight have been identified. This is confirmed by extensive NMR analysis on the labeled patchoulol mixture and comparison with those of unlabeled patchoulol. Deuterium label was located at position C5 (both isotopomers ca. 100%) and at C12 (minor isotopomer, 30–35%). The formation of [5,12-2H2] patchoulol is rationalized through an unknown (so far) hydrocarbon which could incorporate deuterium at C12. This significant observation may have implication on the biosynthesis of nor-patchoulol a congener of patchoulol, the biosynthesis is based on the earlier work [26] (Figure 7).

The interesting observation which can be made on the patchouli oil constituents that though α-guaiene and α-bulnesene are genuine natural products [26], (+)-guaiol and (+)-bulnesol has never been reported to be present in patchouli oil.

2.12. Biosynthesis of Valerenadiene

Pyle et al. [30] reported the first enzymatic synthesis of valerena-4,7(11)-diene (numbering used for valarenic acid) by a unique TPS from *Valeriana officinalis*. They identified two TPS's VoTPS1 and VoTPS2. Transgenic yeast expressing VoTPS1 produced germacrene B and germacrene C and germacrene D. On the other hand, VoTPS2 produced valerena-4,7(11)-diene as a major compound was substantiated by 13CNMR and GC–MS comparison with the synthetic standard. Minor products were identified as bicyclogermacrene and alloaromadendrene. The proposed mechanism involves ring contraction of germacrane ring to a nine-membered intermediate having isobutenyl side chain. Cyclization gives valerena-4,7(11)-diene (Scheme 17).

Yeo et al. [31] proposed a mechanism wherein the isobutyl side chain is derived by the intermediacy of a caryophyllenyl carbocation. A 1,2-hydride shift followed by opening of the cyclobutyl ring. In this way the two methylene carbons of the isobutenyl side chain are predicted to arise from C1 and C11 of the originating FPP and therefore should become labeled when [1-13C] acetate is incorporated into FPP by mevalonate pathway operating in yeast (Scheme 18).

Valerina-1-10-diene and related sesquiterpenes retain an isobutyl side chain whose origin has been recognized as enigmatic because a chemical rationalization for their biosynthesis has not been obvious. They identified seven *Valeriana officinalis*, terpene synthase genes (VoTPSs) and two were functionally characterized as sesquiterpene synthase VoTPS1 and
Scheme 17. Biosynthesis pathway for valerena-4,7(11) diene 47 and other sesquiterpenes from VoTPS1 and VoTPS2.

Scheme 18. Three biosynthetic pathways for valerena-4,7(11) diene 47 and other sesquiterpenes from VoTPS1.
VoTPS7. VoTPS7 encodes for a synthase that biosynthesizes germacrene C \(49\) (90%) whereas VoTPS 1 catalyzes conversion of \(E,E\)-FPP to valerena-1,10-diene \(47\). Overexpression of VoTPS produced valerena-1,10-diene \(47\) on the basis of one and two dimensional NMR analysis, further confirmed by comparison with published spectral data, GC retention time and EIMS fragmentation pattern. The most characteristic feature of the [1-13C] acetate is the FPP derived from the incorporation of [1-13C] acetate had labels located at C1, C3, C5, C7, C9 and C11 as expected using a yeast expression system, specific labeled [1-13C] acetate. FPP was catalytically cyclized (using VoTPS1) and produce valeriana-1,10-diene \(47\) whose 13C labels were found at C3, C5, C7, C9, C1 and C11. Of these C1 and C11 were adjacent carbons of the isobutyl side chain. The proposed mechanism involves an intermediate of a caryophyllenyl carbocation \(53\), 1,2-hydride shift followed by cleavage of C10-C11 bond generates a neutral monocyclic triene \(54\). The proposed scheme also indicates formation of other sesquiterpenes through intermediates tamariscenyl cation \(55\) and valerenyl cation \(56\).

Based on the experimental labeling data of Pyle et al. [30] and Yeo et al. [31], Paknikar et al. [4] proposed a new alternate biosynthetic route (Scheme 19) from IPP to valerenadiene \(47\) which fits the unusual 13C labeling found in valerian and avoids the previously unreported triene \(54\).

In Scheme 19, the 2-1-10-11 sequence of carbons in the first cyclic intermediate \(57\) from \(E,E\)-FPP becomes 2-10-1-11 in valerenadiene \(47\) which fits the 13C labeling pattern formed from [1-13C] acetate [4]. The biosynthetic pathway involves one neutral intermediate; bicyclogermacrene \(36\) found in valerian [32]. The key reaction is a cyclopropylcarbiny1 cation-cyclopropylcarbiny1 cation rearrangement (CCR) analogues to a key reaction in the biosynthesis of squalane from resqualene [3]. Structure interrelationships of the congeners of valerenadiene \(47\) including bicyclogermacrene \(36\), aromadendrene \(51\), germacrene C \(49\), germacrene D \(50\), \(\alpha\)-gurjunene \(58\) and malliol \(59\) were considered in this alternate pathway.

Scheme 19. A cyclopropane route to valerenadiene \(47\) (numbering based on FPP).
Bicyclogermacrene 36 appears also to be an intermediate in the biosynthesis of related set of sesquiterpene with different stereochemistry found in Valeriana officinalis, including tamariscene 60, pacifigorgiol 61 and (+)-pacifigorgia-1,10-diene 62 (Scheme 20). In this scheme also the key reaction is again cyclopropylcarbinyl cation-cyclopropylcarbinyl cation rearrangement (CCR) with this time with a different stereoisomer.

Based on the results of three groups [4, 30, 31] a new consolidated mechanism for the biosynthesis of valerenadiene 47 from FPP via bicyclogermacrene 36 through alloaromadendryl cation 63 and CCR is presented which also explains formation of alloaromadendrene 64 (Scheme 21) replace alloaromadendryl cation with allo-aromadendryl cation.

2.13. Congeners of Xylaria sp.: structural interrelations

Endophytic fungi are reported to produce a number of bioactive metabolites and serve as an excellent source of highly oxygenated compounds which are likely to be potential drugs and also for the applications in crop science. The fungi belonging to genus Xylaria produces plethora of biologically related and structurally fascinating cadinenic and eudesmanic sesquiterpenes.

Liu and coworkers [33] reported isolation of highly oxygenated cadinane based compounds, three new xylaric acid A 65, xylaric acid B 66 and xylaric acid C 67 and nine known compounds xylaric acid D 68, heptelidic acid (avocetlin) [34] 69 hydroheptelidic acid 70, gliocladic acid 71, chlorheptelidic acid 72, trichoderonic acid A 73. The structure assignments are based on extensive spectral analysis. All these congeners belong to cadinane or seco-cadinane group of sesquiterpenes (Figure 8). The stereochemistry at C6 and C7 is unchanged for all the metabolites where C1 remains same for 66, 67, 69, 70, 72 and 73 and changes for 65, 68 and 71.
Scheme 21. Proposed new consolidated mechanism for the biosynthesis of valerenadiene 47.

Figure 8. Structural interrelations among the congeners of Xylaria sp. and the sequence of formation of isolated metabolites 65–73.
Knowing the absolute stereochemistry of the congeners and their fungal origin, they belong to the “antipodal” set of compounds and they can be regarded as a result of extensive oxidative reactions of (−)-γ-cadinene. Recently, Rabe et al. [35] have reported isolation of several sesquiterpenes including (−)-γ-cadinene, [α]_D^25 = −32.3° by incubation of FPP with six purified bacterial terpene cyclases. The results were further supported by labeling experiments with 13C labeled isotopomers of FPP. Interestingly, antipodal cadinenic sesquiterpenes with known absolute configurations have been isolated from Indian vetiver oil (Vetiveria zizanioides) [36]. Isolation of (−)-γ-cadinene, khusinol and khusinol oxide could be regarded as the precursors for the metabolites of Xylaria sp. A very clean sequence indicating a plausible order of formation of Xylaria sp. metabolites associated with the termite nest is presented (Scheme 22). We believe that this presentation will be useful while investigating the biosynthetic pathways using isotopic labeling studies.

3. Conclusions

This chapter gives overview of some of the interesting molecular rearrangements of sesquiterpenes reported over last decade. Further biosynthesis of albaflavenone, caryol-1(11)-ene-10-ol, (+)-koraiol, pogostol, patchouli alcohol and valerenadiene are also presented. The recent trends in the biosynthesis of natural products is focused on enzymatic synthesis using isotopic labeling, nevertheless discussions on structural interrelationships of various congeners provides insights in to natural occurrence of these molecules and finding their biosynthetic links.
Acknowledgements

We wish to dedicate this review to Professor R. B. Bates on his retirement from Research. We thank Dr. Asha D’Souza, Prof. Shailesh Shah and Rahul Chowgule for their valuable help in providing many research articles required for this review.

Author details

Shashikumar K. Paknikar* and Kamlesh Pai Fondekar2

*Address all correspondence to: skpakni@yahoo.co.in

1 Siddharth Chemicals, Kundaim Industrial Estate, Kundaim, Goa, India

2 Deccan Fine Chemicals, Technology and Engineering, Santa Monica Works, Corlim, Goa, India

References


D'Souza AM, Paknikar SK, Dev V, Beauchamp PS, Kamat SP. Biogenetic-type synthesis of (+)-Cymbodiacetal, a constituent of \textit{Cymbopogon martini}. Journal of Natural Products. 2004;67:700-702. DOI: 10.1021/np030338h


Cane DE, Lin X. Biosynthesis of the sesquiterpene antibiotic albaflavenone in \textit{Streptomyces coelicolor}. Mechanism and stereochemistry of the enzymatic formation of epi-isozizaene. Journal of the American Chemical Society. 2009;131:6332-6333. DOI: 10.1021/ja901313v


Khan VA, Gatiillow YV, Dubovenko ZV, Pentegova VA. Crystal structure of koraiol—A sesquiterpene alcohol with a new type of carbon skeleton from the oleoresin of \textit{Pinus


