

Abstract

Sesquiterpenes, a class of biogenic volatile organic compounds, are important precursors to secondary organic aerosols (SOAs) in nature. Using density functional theory (DFT), conceptual DFT, time-dependent (TD) DFT, configuration interaction with single excitation (CIS), and Zerner's intermediate neglect of differential overlap (ZINDO) methods, the electronic structures, spectroscopy, and reactivity of sesquiterpenes were systematically investigated. Results from the CIS calculations show the best consistency in the excited energies and allow for assigning and predicting newly found sesquiterpenes. The results suggest that the first peaks in the ultraviolet-visible (UV-vis) absorption spectra for saturated and unsaturated isomers are $\sigma-\sigma^*$ and $\pi-\pi^*$ transitions, respectively. It can be deduced from the transit intensities of the isomers that an isomer with an endocyclic C = C bond presents weaker UV transition intensity than its corresponding exocyclic isomer. The electronic structures of these compounds were also analyzed by comparing published UV-spectroscopy with advanced theoretical calculations. α -Zingiberene and longicyclene are the most and least reactive in electron-transfer reactions, respectively. No quantitative linear relationships were discovered between the changes in transit energies, DFT chemical reactivity indices of isomers, different degrees of unsaturated C = C double bonds, or the number of substituents attached to the C = C bond. The larger steric hindrance of substituents or exocyclic C = C bond is related directly to higher chemical reactivity possessed by the isomer compared to a corresponding isomer with smaller steric hindrance or with an endo C = C bond. These results are imperative to a better understanding of SOA production mechanisms in the troposphere.

1 Introduction

Secondary organic aerosols (SOAs) are an ubiquitous component of atmospheric particulate matter which has attracted much attention (Went, 1960; Griffin et al., 1999b;

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Jacobson et al., 2000; Wang et al., 2008). The SOAs from the reaction of volatile organic compounds (VOCs) are thought to result from the oxidation of gaseous molecules by one of three electrophilic oxidants present in trace amounts in the atmosphere. The first step in the process of degradation involves the formational mechanism (Grayson, 1998; Chuong et al., 2002; Yao et al., 2006; Blanco et al., 2009). This oxidation process forms gaseous multifunctional, relatively sub-volatile molecules, which contain polar groups like alcohols, carbonyls, organic hydroperoxides, nitrates, and acids etc. (Grayson, 1998; Wisthalera et al., 2001; Lee et al., 2006). These compounds condense over pre-existing particles, leading to the formation of sub-particles (via gas-to-particle).

Sesquiterpenes are the major biogenic VOCs (Heiden et al., 1999) with the general formula $C_{15}H_{24}$. These compounds comprise a large class of terpenes, with approximately 100 representative components found in various vegetative species (Fraga, 2002). They also play a significant role in the formation of SOAs (Kasali et al., 2002), particularly due to their wide commercial applications in odorants, perfumery and plant growth regulators (Wang et al., 2008; Bai and Li, 2008; Krolla and Seinfeld, 2008). These compounds are of special importance because of their high reactivity in the atmosphere, which is measured by their reaction rate constants with the hydroxyl radical ($\cdot OH$), ozone (O_3) and the nitrate radical (NO_3) (Shu and Atkinson, 1995; Pfrang et al., 2006). The reaction of sesquiterpenes with NO_3 , OH or O_3 is dictated by the number of $C=C$ bonds, the number and position of the alkyl-substituent around the $C=C$ bonds (Shu and Atkinson, 1995; Lewin et al., 2001) and the frontier orbitals of the reactants, i.e. the lowest unoccupied molecular orbital (LUMO) of ozone and the highest occupied molecular orbital (HOMO) of sesquiterpenes (King et al., 1999a; Nauduri and Greenberg, 2009).

Unfortunately, the highly variable physical properties associated with short tropospheric lifetimes have led to the great difficulty to obtain complete chemical information on sesquiterpenes (Shu and Atkinson, 1995; Chuong et al., 2002; Cabanas et al., 2006; Pfrang et al., 2006). These obstacles have resulted in an incomplete picture

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of a potentially significant part of atmospheric chemistry and a correspondingly poor experimental understanding of the geophysical and environmental effects of these materials (Novak, 2001; Milosavljevic et al., 2004; Novak and Kovac, 2005; Blanco et al., 2009). In addition, the current theoretical knowledge of many of their basic properties (King et al., 1999b; Milosavljevic et al., 2003) such as ionization cross sections, the appearance energies (AEs), and ultraviolet (UV) transmission spectra (Nauduri and Greenberg, 2009) is limited. Information concerning the relation between the electronic states and atmospheric reactivity of sesquiterpenes is scarce.

The main objectives of the present study were to simulate the ultraviolet-visible (UV-vis) spectra and assign all isomers of 28 common sesquiterpenes recently identified in the environment using configuration interaction with single replacement from reference configurations (CIS) (Pariser and Parr, 1953), time-dependent density functional theory (TDDFT) (Runge and Gross, 1984), Zerner's intermediate neglect of differential overlap (ZINDO) (Zerner, 1991) methodology and conceptual DFT high-level quantum chemical methods. The calculated results were then compared to available experimental data.

2 Conceptual density functional theory and reactivity indices

Parr et al. and other researchers (Parr et al., 1978, 1999; Parr and Pearson, 1983; Xia et al., 2008; Liu, 2009) suggested that DFT methods and reactivity indices are conceptually insightful and practically convenient to predict the chemical reactivity of molecules. It was anticipated that some reactivity indices are equally important for understanding isomeric changes. Chemical potential (μ), one of the reactivity indices, refers to the escaping tendency of electrons from equilibrium and is identified as the negative of electronegativity ($\chi = -\mu$). While chemical hardness (η) measures the resistance to the change in electron density. Several studies have employed these parameters to describe the molecular reactivity by obtaining η and χ values from semi-empirical data, the frontier molecular orbital (FMO) energies.

The theoretical definitions of μ and η are provided by the DFT as the first and second derivatives of the electronic energy with respect to the number of electrons (N) for a constant external potential $V(r)$:

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_v, \eta = \left(\frac{\partial^2 E}{\partial N^2} \right) = \left(\frac{\partial \mu}{\partial N} \right)_v \quad (1)$$

5 The electrophilicity index (ω) derived by Parr et al. (1999) takes the following form:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \quad (2)$$

Based on the finite difference approach method, the working equations for calculating μ and η are given by

$$\mu = -\frac{I + A}{2} \quad (3)$$

10 and

$$\eta = \frac{I - A}{2} \quad (4)$$

where I and A are the first ionization potential and the electron affinity, respectively. Under Koopmans' theorem within the single-determinant wave function approximation such as the Hartree-Fock theory or Kohn-Sham scheme for closed-shell molecules,
15 the above equations can be expressed as

$$\mu = -\frac{\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}}{2} \quad (5)$$

and

$$\eta = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \quad (6)$$

where $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$ designate the energies of the highest occupied and lowest unoccupied molecular orbits, respectively. In addition, two new reactivity indices related

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to electrophilicity and nucleophilicity, as well as electrofugality and nucleofugality in terms of the reactant's first ionization potential (I) and electron affinity (A), have recently been introduced by Ayers et al. (2005). Electrofugality ΔE_e is defined as

$$\Delta E_e \equiv I + \omega = (\mu - \eta)^2 / 2\eta \quad (7)$$

5 Nucleofugality ΔE_n is defined as

$$\Delta E_n \equiv -A + \omega = (\mu + \eta)^2 / 2\eta \quad (8)$$

These equations assess the quality of electron-fleeing and electron-accepting, respectively. These parameters allow us to measure the inherent quality of an isomer, instead of specific effects in a particular reaction environment (Xia et al., 2008).

10 3 Computational details

To obtain information on electronic conformations and energies for the sesquiterpene congeners (Fig. 1), the B3LYP hybrid DFT method with 6–31 G (d, p) basis set was used to optimize molecular geometries of all 28 compounds. In these calculations, fully relaxed minimization was used (symmetry restrictions were excluded during the optimization). Afterwards, harmonic vibrational frequencies were calculated to affirm that the optimized structures are energetic minimums on the potential energy surface (using tight criteria). Spectral calculations were performed using the geometry of a neutral molecule. Excitation energies and oscillator strengths for UV spectra of all target molecules were calculated using CIS, ZINDO and TDDFT within GAUSSIAN03
15 program (Gaussian 03, 2004). All calculations were performed assuming the target
20 molecules were in the gas phase and without solvent effects.

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4 Results and discussion

4.1 Comparison of different methods to describe the UV-vis spectra of sesquiterpenes

Although rigorous theoretical interpretation of UV-vis spectra for molecules as large as sesquiterpenes remains quite challenging (Chuong et al., 2002), reproducing a few lower-energy transitions using computational chemical methods is possible. All these methods are known to be able to produce semi-quantitative agreement with experiments for the transition energies of one-electron excitation. In the present study, the UV-vis spectra of 28 sesquiterpenes were simulated using TDDFT, CIS and ZINDO methods, and 11 simulated spectra were compared with the experimental data from a book (Williams and Fleming, 2009). The transition peaks for isolated double bonds as supplied by this book (Williams and Fleming, 2009) range from 160 to 180 nm. All CIS, TDDFT and ZINDO calculations produced the first six electronic transition states of sesquiterpenes and similar excitation spectra (Table 1).

ZINDO, a semi-empirical method that deals with some aspects of the Hartree-Fock calculation, underestimated the transition energies by greater than 20 nm relative to the experimental data. The transition energies by TD-DFT calculations are systematically overestimated by 1 to 40 nm compared to the standard value for isolated double bonds and by wider margins compared to the values from CIS calculations. Furthermore, the excitation energies of the valence states are relatively well described, but excitation energies with a significant Rydberg character are systematically underestimated by TDDFT calculations (Casida et al., 1998). In comparison with ZINDO and TDDFT, CIS provides the best possible description, with almost all values within the standard range (Williams and Fleming, 2009), of the first peak for these 11 sesquiterpenes under investigation (Table 1). Moreover, CIS calculations obtained reliable characteristic UV-vis absorption spectra for an additional 17 sesquiterpenes (Table 2), and peak assignments were also confirmed through a comparison to available experimental data (Novak, 2001; Novak et al., 2002). This indicates that the lowest energy peak, usually

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well separated from the rest, originates from the excitation of HOMO-orbitals.

4.2 Assignments of theoretical UV absorption

For the sesquiterpene series, the first peak in the UV absorption spectra is associated with $\pi-\pi^*$ transitions because the electronic state with the strongest oscillator strength has a π^* character, except for longicyclene which lacks π double bond in its electronic structure. Furthermore, several additional weaker transitions both from HOMO to higher virtual orbitals and from lower occupied molecular orbitals to LUMO (in the range of 4–11 eV) were obtained by our calculations (Table S1; “S” designates tables and figures in the supplementary data), and these transitions may account for the fine structures observed around the maximum peak in the sesquiterpenes spectra.

In the simulated UV absorption spectrum of longicyclene (Fig. S1), a saturated sesquiterpene, no obvious excited characteristics can be found in the UV-vis range. The first electron transition state is found in the far-ultraviolet region and is assigned a $\sigma-\sigma^*$ electron transition with the largest excitation energy (10.51 eV) and the smallest intensity (0.0017) among all investigated isomers (Table 2).

In the spectra of sesquiterpenes with one double bond and different cyclic arrangements (Fig. S2), the lowest transition energy can be assigned to π -transition (Table 2). Previous studies on methyl-substituted ethenes and terpenoids revealed that π -excitation energy is reduced with increasing number of substituents attached to C = C double bond (Novak et al., 2002). Endocyclic C = C double bonds have a higher degree of alkylation than exocyclic double bonds, and thus their inductive stabilization is weaker than the latter. However, on the whole, not all isomers with endo C = C bonds have lower values of π -excitation energy than those with exo C = C bonds. For example, there are three-substituted C = C double bonds in both α -cedrene and α -cubebene (Fig. 1) with first transition energies of 7.66 and 7.33 eV (Table 2), respectively. The difference between β -cedrene and β -cubebene, both containing a two-substituted C = C bond, is 0.28 eV (Table 2). This suggests that there is no simple relationship between the degree of substitution of the C = C bond and the π -transition

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energy. Therefore, in the discussions of the relative stabilization of π -orbital, it is more accurate to compare a pair of isomers with the same basic structural skeleton rather than with different positions of the C = C double bonds. In other words, comparison of the first excitation energy and UV band intensities is made between isomer pairs: 4-
5 aromadendrene (7.28 eV) and 10-aromadendrene (7.98 eV); α -cedrene (7.67 eV) and β -cedrene (7.99 eV); and α -cubebene (7.33 eV) and β -cubebene (7.71 eV) (Table 2). The evidence in support of the alkylation as the source of π -orbital destabilization can only be found in these pairs. The π -orbitals have higher transition energy in exo than their corresponding endo isomers. The positive deviation of π -transition energy to the
10 latter ranged from 0.70 eV in aromadendrene pairs to 0.14 eV in panasinanene pairs (Table 2). This difference may be due to different basic structures: the hyperconjugation between the C = C double-bond with the σ -orbitals of cyclopropane ring in exo-aromadendrene or the small C–C–C angle at the cyclobutyl in panasinanene.

Based on the comparison of the structures and transition energies for all one un-
15 saturated bond-containing isomers of sesquiterpene, the observed π -transition energy shifts of different isomers can be attributed to variations in the number of alkyl substituents on each C = C bond and in the position of the C = C bond with the same number of alkyl substituents in molecules with the same skeletal structure.

In the spectra of sesquiterpenes with two C = C bonds (Fig. S3), two π -excitation
20 peaks can be expected as observed in previous experiments (Novak, 2001) and found in the current calculations among the first six transition states (Table S1). The nature of the π -excitation can be deduced from CIS calculations and empirical arguments. The assignment of β -caryophyllene can be compared with its epoxide derivative compound without endo C = C bonds, which suggests that lower energy is required for the transition of an endo double bond, meanwhile, higher energy is needed for transition to the exo-C = C bond (Novak, 2001). This is consistent with the results from
25 previous and current theoretical calculations (Table 2). Consequently, it can be deduced that CIS calculations can become a reliable assignment method for unsaturated sesquiterpenes with more than one double bond. The calculated energy differences

between the tri-substituent and di-substituent attached to the double bonds in the same molecule (i.e. -0.19 , -0.43 and -1.03 eV for β -caryophyllene, isocaryophyllene and guaiadiene, respectively; Table 2) further support the conclusion that the number of substituents has an effect on the excitation energy within the same molecule.

For the sesquiterpenes containing three C=C double bond functional groups (Fig. 1), the assignment of each specific band must be attributed to specific π -transition for each double bond. CIS calculations (Table 2) give rise not only to possible energy level patterns, but also to the closeness of orbital energies which can be used for independent confirmation of the assignments.

In the simulation spectrum of α -humulene (Fig. S4), which has three peaks, the transition energies from the fine structure are approximately 7.00 eV. The excitation energy (7.22 eV; Table 2) of π_1 is noticeably lower than those of the other two π -bonds with values of 7.79 and 7.83 eV (Table 2), respectively. Analogously, there are three sharp peaks in the spectrum of bisabolene (Fig. S4). CIS calculations assign the first peak to a four-substituted π_2 bond with a transition energy of 7.47 eV (Table 2). The other two peaks assigned to two three-alkylation C=C double bond functional groups have a small difference between two transition values, i.e. 7.94 eV for π_1 bond and 8.08 eV for π_3 bond (Table 2). This result further confirms that the higher degree of substitution of the double bond requires less π -excitation energy. Finally, the spectrum of α -zingiberene (Fig. S4), specifically, two endo C=C groups among three functional groups, is conjugated and can belong to two characteristic peaks. The result of conjugation lowers the electronic excitation energies and intensity. With an increase in the number of double bonds and formation of a conjugated system, an energy reduction (namely red-shift) will occur due to conjugative stabilization of the excited state when the electron had been ejected from an orbital localized on conjugated double bond. The following discussion will show that the first and third transition peaks with the values of 5.60 and 8.87 eV (Table 2), respectively, can be assigned to the delocalized conjugated double bond. The 7.97 eV peak (Table 2) indicates the excitation of the π -orbital localized along the C=C₃ group.

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4.3 Implications for transition intensity

The transition intensities for the structural pairs with the same skeletons, such as 4-aromadendrene and 10-aromadendrene, α -cedrene and β -cedrene, and α -cubebene and β -cubebene at 0.5853 and 0.6495, 0.4348 and 0.8103, and 0.3212 and 0.9000, respectively (Table 2) based on our calculations, are worth further notice. These results indicate that the exo-double bond in each pair has relatively stronger transition intensity than the endo-double bond. However, the pair of α -panasinsanene (0.6861) and β -panasinsanene (0.6278) (Table 2) is an exception, i.e., the peak of exo-one is weaker than that of endo-one. These data suggest that different intensities may be related to the rigidity of the ring systems, particularly because the endo-double bond somewhat increases the rigidity of a ring. According to the Franck-Condon Principle, a rigid ring system with similar geometries for the ground and excited states has a weak transition intensity. Further evidence supporting this explanation can be found in the transition intensities of sesquicarene which have two peaks corresponding to two types of double bonds. For example, the transition of exo- π_2 -bond (1.1384) is more intense than that of the endo- π_1 -bond (0.4299) (Table 2), although both have three-alkyl groups attached to the C = C bond. Therefore, an isomer with an endocyclic C = C bond presents weak UV transition intensity compared to its corresponding exocyclic one, disregarding any substitution effect.

4.4 Conceptual DFT descriptors of sesquiterpene isomers

The rate for ozonolysis of sesquiterpenes, a major process to produce SOA (Casida et al., 1998; Griffin et al., 1999a; Lee et al., 2006; Winterhalter et al., 2009), is governed by the LUMO of ozone and the HOMO of the sesquiterpenes. Conceptual DFT indexes (μ , η , ω , ΔE_e and ΔE_n) derived from basic density functional theory have been used to investigate static or dynamic inorganic and organic systems. Because η is resistant to deformation or change in donating or withdrawing electrons, μ measures the escaping tendency of electrons from regions with higher μ to areas with lower μ and ω is served

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as a measure of the stabilization energy when atoms or molecules drawing maximal electrons, it is clear that if a molecule has lower η or has a higher absolute value of μ or ω , then the molecule will have higher reactivity and electrophilicity.

As electron donors in electron-transfer interactions with ozone in tropospheric reactions, sesquiterpenes act as reductants with strong nucleophilicity. Initially, higher unsaturated isomers were expected to possess lower chemical hardness and higher electrophilicity index. However, the results from the present study show that the values of all electronic property descriptors have weak correlation to their degree of unsaturation from the calculation at the B3LYP level (Table 3). For example, isocaryophyllene with two C = C bonds has lower η and higher ω values than bisabolene with three C = C bonds (the deviations are -0.13 and 0.10 eV, respectively). It should be noted, however, that α -zingiberene, with three degrees of unsaturation, has the smallest η (5.06) and the largest $|\mu|$ and ω (2.88 and 0.82 eV, respectively) among all isomers under investigation. This means it has a great ability to react with ozone. It also means that this saturated isomer has larger η and lower ω values than unsaturated isomers. For example, longicyclene has the largest η value (8.63 eV) and smallest ω (0.32 eV) among all isomers, indicating its weak reactive ability in electron-transfer reaction.

Moreover, an interesting result arising from our calculations as well as from previous work (Novak et al., 2002) is that the intramolecular position of the double bond within the sesquiterpene skeleton does not govern chemical hardness (η). For example, β -caryophyllene and sesquicarene have different molecular skeletons, although their μ , η , ω , ΔE_n and ΔE_e values are similar. In addition, no direct correlation has been observed between the values of reactive descriptors and the number of alkyl substitutions of unsaturated bonds or the substitution pattern, which is contradictory to the findings of several previous studies (Novak, 2001; Novak et al., 2002; Novak and Kovac, 2005). Successive alkyl substitution results in no gradual and systematic increases in all electronic property indexes, and the magnitude of increase or decrease depends largely on the specific position of a substituent. For instance, α -patchoulene, which has three alkyl groups attached to the C = C bond, has higher η

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and ω values than β -patchoulene (the positive deviations are 0.11 and 0.02 eV, respectively). Although β -caryophyllene and isocaryophyllene are cis-trans isomers with the same alkyl substituents, their μ , η , ω , ΔE_n and ΔE_e values are quite different (the deviations are -0.09 , 0.86 , -0.03 and 0.24 eV, respectively). Rather, the type of double bonds determines the values of μ , η , ω , ΔE_n and ΔE_e . Congeners with an exo C = C bond possess higher chemical reactivity than their corresponding isomers with an endo C = C bond. This can be demonstrated by comparing the chemical hardness values of α -panasinanene ($\eta=6.86$ eV) with β -panasinanene ($\eta=6.94$ eV) and α -cubebene ($\eta=6.58$ eV) with β -cubebene ($\eta=6.67$ eV).

Additionally, the size of a substituent dictates the values of μ , η , ω , ΔE_n and ΔE_e . A molecule with a double bond group attached with a large-size alkyl substituent is more reactive than other isomers. For example, the steric hindrance in longifolene, where two large substituents (i.e. 1,4,8,8-tetramethyldecahydroazulenyl and 4,4,8,8-tetramethyldecahydroazulenyl; Fig. 1) attach to the C = C bond, is larger than that in alloisolongifolene; therefore, longifolene has a smaller η value (the negative deviation is 0.22 eV), i.e., it is less reactive than alloisolongifolene.

5 Conclusions

The present theoretical study obtains the relationship between the electronic states and atmospheric reactivity of sesquiterpenes by examining their UV absorption spectra. Because the reaction of sesquiterpenes with O_3 is the dominant loss process in the atmosphere, the results obtained from the present study are useful for predicting intermediate or final products of secondary and subsequent reactions such as SOA formation from sesquiterpenes.

Supplementary material related to this article is available online at:
[http://www.atmos-chem-phys-discuss.net/10/24325/2010/
acpd-10-24325-2010-supplement.pdf](http://www.atmos-chem-phys-discuss.net/10/24325/2010/acpd-10-24325-2010-supplement.pdf).

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Table 1. Comparison of the UV-excitation energies (nm) of sesquiterpenes based on the TD-B3LYP/6–31G (d, p) and ZINDO levels and the standard value ($\lambda_{\max}=180$ nm) (Williams and Fleming, 2009).

Congeners	λ_{TD}	λ_{ZINDO}	$\Delta\lambda_{\text{T-180}}$	$\Delta\lambda_{\text{Z-180}}$
4-Aromadendrene	202	232	22	52
Longifolene	181	200	1	20
α -Cedrene	184	212	4	32
α -cis-Bergamotene	195	219	15	39
β -Caryophyllene	184	214	4	34
Isocaryophyllene	220	231	40	51
Guaiadiene	203	215	23	35
α -Humulene	222	232	42	52
α -Copaene	192	217	12	37
α -Panasinsanene	182	211	2	31
β -Panasinsanene	183	199	3	19

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Table 2. UV-excitation energy (E_t ; eV), assignments, UV-absorption maxima (λ ; nm) and transition intensity (f) of sesquiterpenes.

Species	E_t	Assignment	λ	f
Longicyclene	10.51	$\sigma-\sigma^*$	117.98	0.0017
4-Aromadendrene	7.28	$\pi-\pi^*$	170.33	0.5853
10-Aromadendrene	7.98	$\pi-\pi^*$	155.45	0.6495
α -Patchoulene	7.53	$\pi-\pi^*$	164.65	0.4196
β -Patchoulene	7.34	$\pi-\pi^*$	168.81	0.3987
α -Cedrene	7.66	$\pi-\pi^*$	161.79	0.4348
β -Cedrene	7.99	$\pi-\pi^*$	155.22	0.8103
α -Cubebene	7.33	$\pi-\pi^*$	169.13	0.3212
β -Cubebene	7.71	$\pi-\pi^*$	160.91	0.9000
Longifolene	7.79	$\pi-\pi^*$	159.23	0.5459
Alloisolongifolene	7.98	$\pi-\pi^*$	155.33	0.5500
α -Panasinanene	7.73	$\pi-\pi^*$	160.29	0.6861
β -Panasinsanene	7.88	$\pi-\pi^*$	157.33	0.6278
Sativene	7.87	$\pi-\pi^*$	157.62	0.6033
Clovene	7.90	$\pi-\pi^*$	156.99	0.5505
α -Copaene	7.39	$\pi-\pi^*$	167.69	0.3354
Thujepsene	7.44	$\pi-\pi^*$	166.72	0.3585
α -cis-Bergamotene	7.40	$\pi-\pi_1^*$	167.61	0.3481
	7.97	$\pi-\pi_2^*$	155.53	1.0178
Sesquicarene	7.95	$\pi-\pi_1^*$	156.03	0.4299
	7.99	$\pi-\pi_2^*$	155.08	1.1384
β -Selinene	8.09	$\pi-\pi_1^*$	153.33	0.7242
	8.17	$\pi-\pi_2^*$	151.71	0.7555
β -Caryophyllene	7.70	$\pi-\pi_1^*$	160.93	0.7876
	7.89	$\pi-\pi_2^*$	157.09	0.4271
Isocaryophyllene	7.33	$\pi-\pi_1^*$	169.24	0.4041
	7.76	$\pi-\pi_2^*$	159.84	0.5794
Guaiadiene	7.27	$\pi-\pi_1^*$	170.55	0.7022
	8.24	$\pi-\pi_2^*$	150.46	0.6329
α -Cadinene	7.64	$\pi-\pi_1^*$	162.19	0.0935
	7.83	$\pi-\pi_2^*$	158.34	1.1315
β -Cadinene	7.68	$\pi-\pi_1^*$	161.44	0.3459
	8.04	$\pi-\pi_2^*$	154.23	0.7628
α -Humulene	7.22	$\pi-\pi_1^*$	171.7	0.1897
	7.79	$\pi-\pi_2^*$	159.11	0.6806
	7.83	$\pi-\pi_3^*$	158.29	0.8969
Bisabolene	7.47	$\pi-\pi_2^*$	165.97	1.2055
	7.94	$\pi-\pi_1^*$	156.19	0.294
	8.08	$\pi-\pi_3^*$	153.39	0.9521
α -Zingiberene	5.60	$\pi-\pi_{1,2}^*$	221.36	0.1838
	7.97	$\pi-\pi_3^*$	155.57	1.1995
	8.87	$\pi-\pi_{1,2}^*$	139.77	0.5712

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Table 3. Calculated conceptual DFT reactivity indices (eV)^a for sesquiterpenes at the B3LYP/6–31 G (d, p) level.

Species	E_{HOMO}	E_{LUMO}	A	I	μ	η	ω	ΔE_{n}	ΔE_{e}
Longicyclene	-6.67	1.96	-1.96	6.67	-2.35	8.63	0.32	2.28	6.99
α -Panasinanene	-5.96	0.90	-0.90	5.96	-2.53	6.86	0.47	1.36	6.43
β -Panasinanene	-6.23	0.71	-0.71	6.23	-2.76	6.94	0.55	1.26	6.78
α -Cubebene	-5.69	0.90	-0.90	5.69	-2.39	6.58	0.44	1.33	6.12
β -Cubebene	-5.93	0.73	-0.73	5.93	-2.60	6.67	0.51	1.24	6.44
α -Patchoulene	-5.85	0.90	-0.90	5.85	-2.48	6.75	0.45	1.35	6.30
β -Patchoulene	-5.71	0.93	-0.93	5.71	-2.39	6.64	0.43	1.36	6.15
α -Cedrene	-6.01	0.87	-0.87	6.01	-2.57	6.88	0.48	1.35	6.49
β -Cedrene	-6.34	0.71	-0.71	6.34	-2.82	7.05	0.56	1.27	6.90
10-Aromadendrene	-6.20	0.79	-0.79	6.20	-2.71	6.99	0.52	1.31	6.73
4-Aromadendrene	-5.69	0.71	-0.71	5.69	-2.49	6.39	0.48	1.19	6.17
Clovene	-6.29	0.82	-0.82	6.29	-2.73	7.1	0.53	1.34	6.81
α -Copaene	-5.88	0.79	-0.79	5.88	-2.54	6.67	0.49	1.27	6.36
Sativene	-6.26	0.71	-0.71	6.26	-2.78	6.97	0.55	1.26	6.81
Thujepsene	-5.90	0.73	-0.73	5.9	-2.58	6.64	0.5	1.24	6.41
Alloisolongifolene	-6.34	0.76	-0.76	6.34	-2.79	7.1	0.55	1.31	6.89
Longifolene	-6.23	0.65	-0.65	6.23	-2.79	6.88	0.56	1.22	6.80
β -Caryophyllene	-6.34	0.71	-0.71	6.34	-2.82	7.05	0.56	1.27	6.90
Isocaryophyllene	-5.93	0.44	-0.44	5.93	-2.75	6.37	0.59	1.03	6.52
α -Cadinene	-5.99	0.73	-0.73	5.99	-2.63	6.72	0.51	1.25	6.50
β -Cadinene	-6.10	0.84	-0.84	6.10	-2.63	6.94	0.50	1.34	6.59
Guaiadiene	-6.07	0.49	-0.49	6.07	-2.79	6.56	0.59	1.08	6.66
β -Selinene	-6.45	0.73	-0.73	6.45	-2.86	7.18	0.57	1.30	7.02
Sesquicarene	-6.07	0.93	-0.93	6.07	-2.57	6.99	0.47	1.40	6.54
α -cis-Bergamotene	-5.90	0.76	-0.76	5.90	-2.57	6.67	0.5	1.26	6.4
α -Humulene	-5.80	0.60	-0.60	5.80	-2.60	6.39	0.53	1.13	6.32
Bisabolene	-5.77	0.73	-0.73	5.77	-2.52	6.50	0.49	1.22	6.26
α -Zingiberene	-5.41	-0.35	0.35	5.41	-2.88	5.06	0.82	0.47	6.24

^a E_{HOMO} : the highest occupied molecular orbital (HOMO) energy; E_{LUMO} : the lowest unoccupied molecular orbital (LUMO) energy; I : first ionization energy; A : electron affinity; μ : chemical potential; η : chemical hardness; ω : electrophilicity index; ΔE_{n} : nucleofugality; ΔE_{e} : electrofugality.

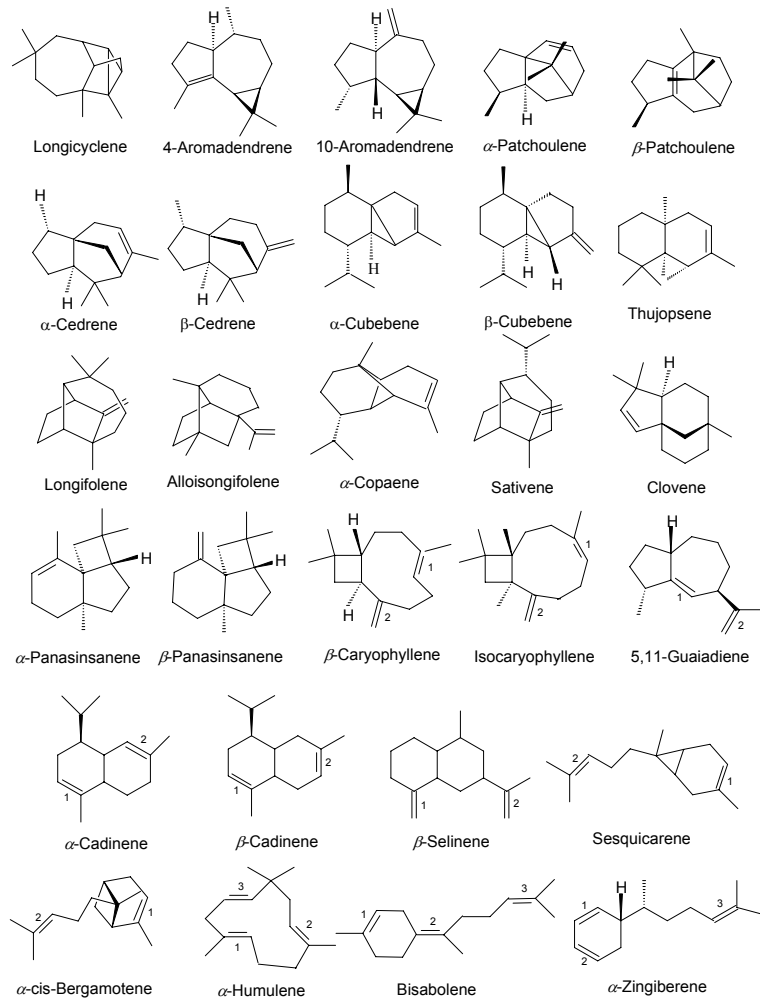


Fig. 1. Structures of the target sesquiterpenes under investigation.
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