

High-level G4 and G4(MP2) theoretical study into the gas-phase thermodynamic and electronic properties of atmospherically relevant terrestrial vegetation derived C₁₀H₁₆ monoterpenes and C₁₅H₂₄ sesquiterpenes

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Abstract

High-level G4 and G4(MP2) calculations were completed on 74 atmospherically relevant monoterpene and sesquiterpene hydrocarbons derived from terrestrial vegetation. Gas-phase standard state enthalpies of formation ($\Delta_f H^\circ(g)$) were calculated, along with enthalpies of isomerization ($\Delta_{\text{isom}} H^\circ(g)$) and both gas-phase standard state 298.15 K and 0 K adiabatic ionization energies (AIEs). The G4 and G4(MP2) methods yield highly self-consistent results, with G4(MP2) $\Delta_f H^\circ(g)$, $\Delta_{\text{isom}} H^\circ(g)$, and AIE systematically lower than G4 values by several kJ mol⁻¹. Calculated $\Delta_f H^\circ(g)$ are in good agreement with limited available experimental data, indicating effective thermochemical accuracy. Stability trends broadly adhere to Zaitsev's rule, with endocyclic, more highly substituted double bonds conferring a thermodynamic advantage over their exocyclic, less substituted counterparts. Compact, highly bridged polycyclic frameworks emerge as the most stable motifs by efficiently distributing structural strain. G4 and G4(MP2) calculated AIEs – also within effective thermochemical accuracy – are governed by π -conjugation, alkene–cyclopropyl orbital interactions, and alkyl substitution.

1. Introduction

Biogenic volatile organic compounds (BVOCs) emitted by terrestrial vegetation constitute a substantial flux of reactive carbon into the troposphere, governing global tropospheric chemistry, the oxidizing capacity of the lower atmosphere, and the global carbon cycle [1, 2]. Although isoprene is generally recognized as the largest individual BVOC emission source globally, monoterpenes (C₁₀H₁₆) and sesquiterpenes (C₁₅H₂₄) represent two of the most atmospherically significant classes of biogenic hydrocarbons [3–6]. Their environmental importance stems primarily from their high atmospheric reactivities toward major tropospheric oxidants, namely the hydroxyl radical ($\cdot\text{OH}$), ozone (O₃), and the nitrate radical ($\cdot\text{NO}_3$), as well as their complex, multifunctional oxidation chemistry that drives the formation of highly oxygenated organic molecules and secondary organic aerosols (SOAs) [7, 8]. These biogenic SOAs play a vital role in climate regulation by acting as cloud condensation nuclei and contributing to new particle formation, thereby influencing the Earth's radiative balance [9–12].

Despite the profound environmental impacts of these compounds, evaluating their atmospheric degradation pathways and multiphase chemical transport remains a significant challenge due to a lack of high-quality fundamental thermodynamic data. Monoterpenes and sesquiterpenes exhibit substantial structural diversity, encompassing numerous constitutional and stereoisomers with acyclic, monocyclic, bicyclic, and tricyclic frameworks [13–17]. Reliable experimental or calculated gas-phase thermochemical data, such as standard state enthalpies of formation ($\Delta_f H^\circ(g)$) and enthalpies of isomerization ($\Delta_{\text{isom}} H^\circ(g)$), remain scarce. This deficiency is particularly acute for the vast majority of sesquiterpene isomers, which are often unstable, occur at low ambient abundances, or possess highly complex structural topologies that preclude straightforward isolation and direct experimental measurement. In addition to core gas-phase thermochemistry, characterizing fundamental electronic properties such as ionization energies (IE) is essential for modern atmospheric monitoring and structural analysis. Ionization potentials serve as critical descriptors for predicting gas-phase reactivities via structure–activity relationships, as the energy of the highest occupied molecular orbital correlates strongly with the rate of electrophilic attack by atmospheric scavengers [18–21].

To resolve these data gaps, high-accuracy composite ab initio quantum-chemical protocols offer a powerful alternative to experiment, routinely achieving chemical accuracy (within ± 1 kcal/mol [± 4.2 kJ mol⁻¹]) for molecular systems of this scale. Among these, the Gaussian-4 (G4) [22] and the computationally optimized Gaussian-4 modified second-order Møller-Plesset perturbation theory (G4(MP2)) [23] methods developed by Curtiss and co-workers represent state-of-the-art benchmarks for gas-phase thermochemical properties and electronic energies. While density functional theory (DFT) formalisms have been widely used to explore localized sets of monoterpenes and sesquiterpenes, systematic high-level composite ab initio treatments targeting thermodynamic metrics across extensive isomeric suites remain rare in the literature.

In this work, we deploy high-level G4 and G4(MP2) model chemistries to systematically determine the gas-phase thermodynamic and electronic profiles for an extensive suite of atmospherically relevant monoterpenes and sesquiterpenes derived from terrestrial vegetation, comprising 20 monoterpene isomers and 54 sesquiterpene isomers (n=74 total). Using these composite ab initio frameworks, we calculate gas-phase standard enthalpies of formation, enthalpies of isomerization, and adiabatic ionization energies. The resulting self-consistent dataset is compared against available experimental reference data to assess model performance across diverse structural classes, ranging from acyclic chains to highly strained polycyclic systems. Ultimately, this comprehensive data suite is intended to resolve long-standing ambiguities in terpene thermochemistry, evaluate the internal consistency of proposed atmospheric oxidation mechanisms, and provide accurate structural and energetic reference inputs required for atmospheric kinetic modeling and aerosol yield parameterizations.

2. Computational Methods

The initial three-dimensional molecular structures for all compounds were retrieved from the PubChem database [24], imported into Avogadro v.1.2.0 and v.2.0.0 [25], and checked for accuracy. To ensure a comprehensive mapping of the low-energy potential energy surface for each

compound, a rigid molecular mechanics conformer systematic rotor search was performed using the MMFF94 force field [26–32] conducted using a steepest descent algorithm over 500 iterations with convergence threshold of 10^{-7} within the Avogadro software environment.

The resulting minimum-energy conformers identified for each compound were subsequently subjected to high-level quantum-chemical calculations using the composite Gaussian-4 (G4) [22] and Gaussian-4 modified second-order Møller-Plesset perturbation theory (G4(MP2)) [23] model chemistries within the Gaussian 16 program package [33] on the clusters of the Digital Research Alliance of Canada grid. No compounds contained imaginary frequencies at the final optimized geometry. Only the lowest energy conformation of each compound was considered for further analysis and discussion. Molecular geometries were visualized using Gabedit v.2.5.1 [34] and Avogadro v.1.2.0 and v.2.0.0 [25]. Statistical analyses were conducted using KyPlot v.6.0.2 [35]. Two-dimensional compound structures were drafted using KingDraw v.3.0.2.En_us [36].

Gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of formation ($\Delta_f H^\circ_{(g)}$) were calculated via the atomization approach [37–39] with the following experimental atomic $\Delta_f H^\circ_{(g)}$ (values in kJ mol^{-1}): H, $+217.998 \pm 0.006$; C, $+716.68 \pm 0.45$. This choice of method and composite model frameworks is supported by previous benchmarking and validation efforts using the G4 and G4(MP2) methods, which demonstrated that the atomization approach routinely provides excellent agreement with experimental references across an extensive suite of organic and inorganic compounds, including structurally strained, polycyclic, and functionalized frameworks [39–49]. Gas phase standard state (298.15 K, 1.01325 bar [1 atm]) and 0 K adiabatic ionization energies (AIEs; AIE_{298K} and AIE_{0K}, respectively) were calculated as described elsewhere [50]. Similar to $\Delta_f H^\circ_{(g)}$ calculations, estimated AIEs using the G4 and G4(MP2) methods have been subjected to extensive benchmarking and shown to provide results at or near thermochemical accuracy for a wide range of compounds [41, 43, 50].

3. Results and Discussion

G4 and G4(MP2) calculated $\Delta_f H^\circ_{(g)}$ and $\Delta_{\text{isom}} H^\circ_{(g)}$ for the monoterpenes (Figure 1) and sesquiterpenes (Figures 2 through 4) reveal a broad range within each class (Tables 1 and 2). Only camphene (**2**) and α -carene (3-carene/ Δ^3 -carene; **9**) appear to have gas-phase experimental $\Delta_f H^\circ_{(g)}$ in the NIST Chemistry WebBook [51]. Camphene (**2**) has a reported $\Delta_f H^\circ_{(g)}$ of $-28 \pm 2 \text{ kJ mol}^{-1}$ [52] that is in excellent agreement with the G4 ($-25.0 \text{ kJ mol}^{-1}$; $\Delta = +3.0 \text{ kJ mol}^{-1}$) and G4(MP2) ($-26.9 \text{ kJ mol}^{-1}$; $\Delta = +1.1 \text{ kJ mol}^{-1}$) calculations. Similarly, α -carene (**9**) has a reported $\Delta_f H^\circ_{(g)}$ of $+19 \pm 4 \text{ kJ mol}^{-1}$ from ref. [53] that agrees well with the G4 ($+24.3 \text{ kJ mol}^{-1}$; $\Delta = +5.3 \text{ kJ mol}^{-1}$) and G4(MP2) ($+22.6 \text{ kJ mol}^{-1}$; $\Delta = +3.6 \text{ kJ mol}^{-1}$) values.

From the remaining compounds, experimental $\Delta_f H^\circ_{(g)}$ can be derived ($\Delta_f H^\circ_{(g),\text{der}}$) from the condensed phase thermochemistry data (liquid-phase standard state (298.15 K) enthalpies of formation ($\Delta_f H^\circ_{(l)}$) and the liquid-to-vapor phase change data (standard state (298.15 K) enthalpies of vaporization ($\Delta_{\text{vap}} H^\circ$)) for five compounds (Table 3). Good agreement was observed between these $\Delta_f H^\circ_{(g),\text{der}}$ and the G4/G4(MP2) calculated $\Delta_f H^\circ_{(g)}$ with the exception of β -myrcene (**16**), for which the experimental $\Delta_f H^\circ_{(l)}$ is in doubt. Our $\Delta_f H^\circ_{(g),\text{der}}$ for α -pinene (**13**; $+28.2 \pm 3.0 \text{ kJ mol}^{-1}$) and β -pinene (**18**; $+38.1 \pm 3.0 \text{ kJ mol}^{-1}$) are also in excellent agreement with another report of $+30.2$ and $+35.8 \text{ kJ mol}^{-1}$, respectively [54]. Overall, this suggests a maintenance of effective G4/G4(MP2) computational chemical accuracy ($\pm 4.2 \text{ kJ mol}^{-1}$) for these classes of structurally diverse and complex natural products.

Prior G4 and G4(MP2) calculations using the atomization method for a subset of the compounds under study also agree well with the values presented herein. G4/G4(MP2) $\Delta_f H^\circ_{(g)}$ from ref. [55] are as follows, with the current study's G4/G4(MP2) values in brackets for comparison (all values in kJ mol^{-1}): camphene (**2**), $-28.4/-30.3$ [$-25.0/-26.9$]; α -terpinene (**14**), $-18.5/-21.3$ [$-15.0/-17.9$]; bornylene (**1**), $-17.1/-19.4$ [$-13.7/-16.0$]; γ -terpinene (**20**), $-13.8/-16.9$ [$-8.6/-12.2$]; β -phellandrene (**17**), $-6.8/-10.9$ [$-3.3/-7.5$]; α -phellandrene (**12**), $-3.8/-7.6$ [$-1.6/-5.6$]; limonene (**3**), $-2.4/-5.8$ [$+1.9/-1.9$]; terpinolene (**5**), $-2.4/-5.3$ [$+1.1/-1.9$]; α -carene (**9**), $+20.9/+19.2$ [$+24.3/+22.6$]; α -pinene (**13**), $+22.9/+20.8$ [$+26.4/+24.3$]; α -thujene (**15**), $+25.7/+24.4$ [$+29.2/+27.9$]; sabinene (**4**), $+32.4/+31.1$ [$+35.9/+34.6$]; β -pinene (**18**), $+33.2/+31.1$ [$+36.7/+34.5$]; and β -myrcene (**16**), $+75.2/+69.9$ [$+78.6/+73.4$]. These prior G4/G4(MP2) values are systematically lower than the current work by $\sim 3.5 \text{ kJ mol}^{-1}$. The reason for this difference is unknown, although the atomization G4/G4(MP2) $\Delta_f H^\circ_{(g)}$ from ref. [55] were observed to be systematically lower than the experimental $\Delta_f H^\circ_{(g)}$ the authors benchmarked against in this prior study, and were corrected upwards. However, because the differences in G4/G4(MP2) $\Delta_f H^\circ_{(g)}$ between ref. [55] and the current work is consistently and precisely systematic, the inferred $\Delta_{\text{isom}} H^\circ_{(g)}$ between this previous work and the present study are effectively equivalent, further validating the data quality herein.

G4(MP2) $\Delta_f H^\circ_{(g)}$ from ref. [56] are as follows, with the current study's G4/G4(MP2) values in brackets for comparison (all values in kJ mol^{-1}): camphene (**2**), -30.0 [$-25.0/-26.9$]; γ -terpinene (**20**), -15.4 [$-8.6/-12.2$]; terpinolene (**5**), -5.1 [$+1.1/-1.9$]; limonene (**3**), -3.7 [$+1.9/-1.9$]; α -carene (**9**), $+19.5$ [$+24.3/+22.6$]; β -pinene (**18**), $+21.1$ [$+36.7/+34.5$]; α -pinene (**13**), $+31.5$ [$+26.4/+24.3$]; and sabinene (**4**), $+34.6$ [$+35.9/+34.6$]. There is variability between the G4(MP2) $\Delta_f H^\circ_{(g)}$ from ref. [56] and those reported at the same level using the atomization method in ref. [55] and in the

present work. G4(MP2) $\Delta_f H^\circ_{(g)}$ for camphene (**2**), α -carene (**9**), and terpinolene (**5**) are in excellent agreement (0.2–0.3 kJ mol⁻¹ difference) between ref. [56] and ref. [55], whereas $\Delta_f H^\circ_{(g)}$ for sabinene (**4**) agrees perfectly between ref. [56] and the current work. There are inconsistent differences between the $\Delta_f H^\circ_{(g)}$ for α -pinene (**13**), β -pinene (**18**), limonene (**3**), and γ -terpinene (**20**) between ref. [56] and either ref. [55] or the current work. For limonene (**3**) and γ -terpinene (**20**), the variation between the G4(MP2) $\Delta_f H^\circ_{(g)}$ from ref. [56] and these other two studies is small (≤ 2 –3 kJ mol⁻¹).

On the other hand, for α - and β -pinene, the differences are too substantial (7.2–10.7 and 10.0–13.4 kJ mol⁻¹, respectively) to be a result of conformational variability or subtle variations in the application of the atomization approach. According to the data in ref. [56], the isomerization of α - to β -pinene should be exothermic by -10.4 kJ mol⁻¹ at the G4(MP2) level. However, the C=C double bond in β -pinene (**18**) is exocyclic and should be less thermodynamically favored than the endocyclic C=C double bond in α -pinene (**13**). Thus, the isomerization of α - to β -pinene should be endothermic, as the G4(MP2) $\Delta_{\text{isom}} H^\circ_{(g)}$ results from the current work (+10.2 kJ mol⁻¹) and ref. [55] (+10.3 kJ mol⁻¹) show. Consequently, it is possible that the structures of α - and β -pinene were interchanged in this prior work, resulting in the differing thermodynamic stability ranking for these two compounds than is expected and which previous and the current G4/G4(MP2) investigations demonstrate.

Some group contribution methods (GCMs) provide widely differing and sometimes erroneous results for these compound classes, illustrating the need for accurate high-level calculations. For example, the Joback-Reid (JR), Constantinou-Gani (CG), and Benson (B*) GCMs gave $\Delta_f H^\circ_{(g)}$ of -69.1, +19.8, and +28.3 kJ mol⁻¹ for α -pinene (**13**) [57], compared to the G4/G4(MP2) $\Delta_f H^\circ_{(g)}$ of +26.4/+24.3 kJ mol⁻¹. Similarly, the JR, CG, and B* $\Delta_f H^\circ_{(g)}$ were -31.2, +26.2, and +38.7 kJ for β -pinene (**18**) [57], versus the G4/G4(MP2) $\Delta_f H^\circ_{(g)}$ of +36.7/+34.5 kJ mol⁻¹. The $\Delta_{\text{isom}} H^\circ_{(g)}$ for the α - to β -pinene isomerization for the JR, CG, and B* methods is thus +37.9, +6.4, and +10.4 kJ mol⁻¹, respectively, versus +10.3/+10.2 kJ mol⁻¹ at the G4/G4(MP2) levels. The Stein and Brown group-additivity (SB) method was also deployed, along with modified B3LYP/6-31G(d,p) approaches (designated M1 and M2) to estimate the $\Delta_f H^\circ_{(g)}$ for a group of monoterpenes, resulting in the following values (presented as SB/M1/M2 where "nc" represents values not calculated by these authors; all values in kJ mol⁻¹; current study G4/G4(MP2) results in brackets) [58]: camphene (**2**), nc/-5.9/-19.2 [-25.0/-26.9]; α -terpinene (**14**), +5.4/nc/-10.5 [-15.0/-17.9]; γ -terpinene (**20**), +11.7/nc/-9.2 [-8.6/-12.2]; terpinolene (**5**), +20.1/nc/nc [+1.1/-1.9]; limonene (**3**), +28.9–34.3/nc/+2.9 [+1.9/-1.9]; α -pinene (**13**), nc/+35.1/nc [+26.4/+24.3]; sabinene (**4**), nc/+38.1/nc [+35.9/+34.6]; β -pinene (**18**), nc/+49.4/+49.0 [+36.7/+34.5]; and β -myrcene (**16**), +103.8/nc/+76.1 [+78.6/+73.4].

$\Delta_f H^\circ_{(g)}$ for the monoterpenes range from -25.3 kJ mol⁻¹ (G4) for tricyclene (**8**) and -26.9 kJ mol⁻¹ (G4(MP2)) for camphene (**2**) to +79.8/+74.6 kJ mol⁻¹ for α -ocimene (**11**). $\Delta_f H^\circ_{(g)}$ for the sesquiterpenes range from -142.2/-143.4 kJ mol⁻¹ (G4/G4(MP2)) for β -patchoulene (**74**) to +80.4/+73.7 kJ mol⁻¹ (G4/G4(MP2)) for β -farnesene (**22**), yielding a $\Delta_{\text{isom}} H^\circ_{(g)}$ range of +222.6/+217.2 kJ mol⁻¹ (G4/G4(MP2)). A comparison of the calculated $\Delta_f H^\circ_{(g)}$ and $\Delta_{\text{isom}} H^\circ_{(g)}$ at the G4 and G4(MP2) composite levels reveals close agreement across all 74 monoterpenes and sesquiterpenes examined (Figure 5). For the full dataset, the deviations between $\Delta_{\text{isom}} H^\circ_{(g)}$ ($\Delta_{\text{isom}} H^\circ_{(g),G4(MP2)-G4}$) at the two levels do not exceed 5.4 kJ mol⁻¹, with the largest discrepancies arising in the conformationally flexible acyclic polyenes (e.g., α - (**21**; $\Delta_{\text{isom}} H^\circ_{(g),G4(MP2)-G4} = -5.2$ kJ mol⁻¹) and β -farnesene (**22**; $\Delta_{\text{isom}} H^\circ_{(g),G4(MP2)-G4} = -5.4$ kJ mol⁻¹)). G4(MP2) $\Delta_f H^\circ_{(g)}$ values are systematically lower than the comparison G4 $\Delta_f H^\circ_{(g)}$ values, with the corresponding $\Delta \Delta_f H^\circ_{(g),G4(MP2)-G4}$ ranging from -0.2 to -5.3 kJ mol⁻¹ for the monoterpenes and -0.9 to -6.6 kJ mol⁻¹ for the sesquiterpenes.

The $\Delta_{\text{isom}} H^\circ_{(g)}$ values provide a direct measure of relative thermodynamic stability, referencing the lowest-enthalpy isomer at each level of theory. Overall, the G4 and G4(MP2) methods yield highly consistent structural rankings and energetic values, with only minor variations among closely degenerate states. The monoterpenes investigated exhibit a broad structural diversity, ranging from acyclic trienes to complex bridged tricyclic frameworks. This structural variance results in a significant thermodynamic spread, with the least stable isomer, α -ocimene (11**), residing +105.1/+101.5 kJ mol⁻¹ (G4/G4(MP2)) above the global minimum.**

The data demonstrates a clear energetic penalty associated with acyclic, open-chain structures. The acyclic trienes, trans,trans-alloocimene (**7**), trans- β -ocimene (**6**), β -myrcene (**16**), and α -ocimene (**11**), are the least thermodynamically stable compounds in the dataset, occupying ranks 17 through 20, reflecting the thermodynamic penalty associated with the lack of ring-stabilizing cyclization. Trans,trans-alloocimene (**7**) has an extended fully conjugated π -system across all three of its double bonds. The resulting delocalization energy provides a

thermodynamic stabilization of +32.7/+32.2 to +35.9/+35.2 kJ mol⁻¹ (G4/G4(MP2)) compared to its doubly conjugated counterparts (**6**, **16**, and **11**), which are effectively isoenthalpic within the error of calculation (± 4.2 kJ mol⁻¹).

Cyclization substantially improves thermodynamic stability, though the degree of stabilization is highly dependent on ring strain and the positioning of the double bonds. Among the monocyclic menthadienes, conjugated systems are energetically favored. α -terpinene (**14**), a conjugated diene, is favored over the structurally similar isolated diene γ -terpinene (**20**) by +6.4/+5.7 kJ mol⁻¹ at the G4/G4(MP2) levels. The stabilization afforded by higher substitution on endocyclic double bonds is illustrated when comparing structurally similar bicyclic pairs. For example, α -pinene (**13**), featuring an endocyclic double bond, is more stable than its exocyclic isomer, β -pinene (**18**), by +10.3/+10.2 kJ mol⁻¹ (G4/G4(MP2)).

Bicyclic systems fusing a six-membered ring with a highly strained three- or four-membered ring, such as the cyclobutane ring in the pinenes (**13**, **18**) or the cyclopropane rings in α -carene (**9**), sabinene (**4**), and the thujenes (**15**, **19**), cluster in the intermediate stability ranks (11 through 16). The inherent ring strain of these fused systems partially counteracts the stabilization typically gained from cyclization. The lowest-enthalpy structural motifs are characterized by compact, highly bridged architectures. Tricyclene (**8**), camphene (**2**), and α -fenchene (**10**) rank as the three most stable monoterpenes and are isoenthalpic within the error of calculation. The absence of π -bonds in tricyclene's tricyclic structure (**8**) allows it to maximize the number of stronger σ -bonds, an enthalpic advantage that overcomes its intrinsic cage strain.

The substitution-dependent hyperconjugative stabilization underpinning the alkene trends discussed above also operates in the saturated skeletons. Whereas alkyl substitution of a π -bond stabilizes the system through $\sigma \rightarrow \pi^*$ donation (the thermodynamic basis of Zaitsev selectivity), an analogous $\sigma \rightarrow \sigma^*$ donation arises in branched carbon frameworks, where each tertiary or quaternary center increases the number of through-bond donor-acceptor interactions. Tricyclene (**8**) exemplifies this limit, incorporating two quaternary and three tertiary carbons within a compact cage, and is effectively isoenergetic with camphene (**2**), whose single quaternary center and exocyclic methylene leave the sp³ skeleton less densely substituted. In the unsaturated series, this substitution hierarchy similarly contributes to the ordering within constitutionally matched pairs, including γ -terpinene (**20**) versus α -phellandrene (**12**) and α -thujene (**15**) versus β -thujene (**19**), although in these cases substitution effects are superimposed on conjugation and endocyclic/exocyclic alkene placement. Finally, the cyclopropane Walsh orbitals of tricyclene (**8**) constitute particularly effective σ -donors, delocalizing electron density through the adjacent cage σ -framework and reinforcing the unusually high stability of this saturated tricycle.

For the sesquiterpenes, the acyclic isomers, α -farnesene (**21**) and β -farnesene (**22**), exhibit the highest $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ at +218.8/+213.6 kJ mol⁻¹ and +222.6/+217.2 kJ mol⁻¹, respectively, at the G4 and G4(MP2) levels, designating them as the least thermodynamically stable compounds in the dataset. Macrocyclic and monocyclic frameworks, such as the germacrenes (**23** through **26**), display intermediate stabilities with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ ranging between +164.2/+160.0 and +181.7/+177.4 kJ mol⁻¹ (G4/G4(MP2)).

Maximum thermodynamic stability is achieved within compact, polycyclic frameworks where ring strain is minimized and transannular dispersive contacts are maximized. Across both composite quantum chemical methods, β -patchoulene (**74**) represents the global minimum, serving as the reference zero-point for isomerization enthalpy (0.0 kJ mol⁻¹). Its rigid, fused tricyclic architecture efficiently distributes structural strain. Other highly stable tricyclic structures include isolongifolene (**61**) and α -cedrene (**64**), which lie merely +9.8/+10.1 kJ mol⁻¹ and +9.9/+9.6 kJ mol⁻¹, respectively (G4/G4(MP2)) above β -patchoulene. Bicyclic systems, including the cadinenes, muurolenes, and selinenes, populate intermediate to high stability rankings, with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ generally ranging from $\sim +48$ to $\sim +66$ kJ mol⁻¹ depending on level of theory.

Within specific skeletal classes, and as is also evident within the monoterpene dataset, the position and degree of substitution of double bonds play a central role in dictating thermodynamic preference, adhering strictly to Zaitsev's rule. Endocyclic double bonds consistently furnish greater thermodynamic stability relative to their exocyclic counterparts. In the cedrene framework, the endocyclic double bond in α -cedrene (**64**) stabilizes the molecule by +14.5/+14.5 kJ mol⁻¹ (G4/G4(MP2)) relative to the exocyclic double bond in β -cedrene (**70**). Similarly, among the bicyclic selinene isomers, endocyclic α -selinene (**45**) is favored over exocyclic β -selinene (**52**) by +3.4/+3.5 kJ mol⁻¹ (G4/G4(MP2)) and endocyclic α -cadinene (**40**) is favored over exocyclic γ -cadinene (**53**) by +3.2/+3.3 kJ mol⁻¹ (G4/G4(MP2)).

A detailed examination of stereoisomeric pairs underscores the significant energetic impact of ring-junction configurations and side-chain orientations on identical carbon frames. In the cyclopropahydroazulene system, aromadendrene (**60**) exhibits an $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ of +121.4/+120.7 kJ mol⁻¹ (G4/G4(MP2)), whereas its epimer alloaromadendrene (**59**) is destabilized to +130.2/+130.1 kJ mol⁻¹ (G4/G4(MP2)). This ~ 9 kJ mol⁻¹ destabilization in alloaromadendrene stems from transannular strain and unfavorable steric interactions across the fused cyclopropane ring junction. Conversely, the diastereomeric tricyclics ylangene (**63**) and α -copaene (**65**) exhibit near energetic equivalence, with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ of +87.8/+86.8 kJ mol⁻¹ (G4/G4(MP2)) and +88.7/+87.7 (G4/G4(MP2)), respectively. The minor 0.9 kJ mol⁻¹ difference indicates that

stereochemical inversion at peripheral bridgehead sites induces negligible steric congestion. Furthermore, among bicyclic cadinane-type skeletons, ring-junction stereochemistry substantially shifts stability rankings: α -amorphene (**39**, $\Delta_{\text{isom}}H^\circ_{(\text{g})}=+51.6/+49.2 \text{ kJ mol}^{-1}$ (G4/G4(MP2)) and α -muurolene (**44**, $\Delta_{\text{isom}}H^\circ_{(\text{g})}=+51.6/+49.5 \text{ kJ mol}^{-1}$ (G4/G4(MP2))) are more stable than α -cadinene (**40**, $\Delta_{\text{isom}}H^\circ_{(\text{g})}=+60.6/+57.8 \text{ kJ mol}^{-1}$ (G4/G4(MP2))) by approximately +8.3 to +9.0 kJ mol^{-1} , demonstrating the role of decalyl ring-fusion stereochemistry in relieving nonbonded repulsion.

Methodologically, comparing G4 and G4(MP2) calculations reveals systematic trends tied to structural flexibility. For rigid, compact polycyclic isomers such as isolongifolene (**61**), both methods yield nearly identical $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ results, differing by only 0.3 kJ mol^{-1} (+9.8 kJ mol^{-1} for G4 versus +10.1 kJ mol^{-1} for G4(MP2)). However, for highly flexible, acyclic architectures, the gap widens significantly. For β -farnesene (**22**), G4(MP2) predicts an isomerization enthalpy 5.4 kJ mol^{-1} lower than G4 (+217.2 kJ mol^{-1} versus +222.6 kJ mol^{-1}). This behavior indicates that while G4(MP2) provides an efficient and accurate approximation for rigid ring systems, it slightly underestimates relative instability in highly flexible, open-chain isomers compared to the full G4 protocol.

Some density functional theory (DFT) methods have difficulty with the correct thermodynamic rank ordering and magnitude of isomerizations within the monoterpenes and sesquiterpenes. This is a well-known issue for organic compounds, regardless of the nature of substituents or structural motifs [59–67], necessitating either carefully chosen and benchmarked density functionals or, preferably, a move to high-level composite methods and their equivalent. For example, work at the B3LYP/6-31G(d) level found the following thermodynamic stability order (with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ in brackets in kJ mol^{-1}) for various monoterpenes [68]: α -terpinene (**14**) [0.0] > terpinolene (**5**) [+12.2] > limonene (**3**) [+25.0] > camphene (**2**) [+27.5] > α -fenchene (**10**) [+30.4] > tricyclene (**8**) [+32.4] > bornylene (**1**) [+49.5] > α -pinene (**13**) [+68.6] > sabinene (**4**) [+75.3] > α -carene (**9**) [+155.5]. The G4/G4(MP2) order from the current work (with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ in brackets in kJ mol^{-1} ; normalized to tricyclene (**8**) for both methods although G4(MP2) ranks camphene (**2**) as most thermodynamically stable) for this group of compounds is tricyclene (**8**) [0.0/0.0] > camphene (**2**) [+0.3/-1.4] > α -fenchene (**10**) [+1.4/-0.6] > α -terpinene (**14**) [+10.3/+7.6] > bornylene (**1**) [+11.6/+9.5] > terpinolene (**5**) [+26.4/+23.6] > limonene (**3**) [+27.2/+23.6] > α -carene (**9**) [+49.6/48.1] > α -pinene (**13**) [+51.7/+49.8] > sabinene (**4**) [+61.2/+60.1]. Without the quantitative results, the rank orders are **14>5>3>2>10>8>1>13>4>9** for the prior work versus **8>2>10>14>1>5>3>9>13>4** for the current G4/G4(MP2) study.

Similarly, a B3LYP/6-31G(d, p)// B3LYP/6-311G(2d, 2p) study reported the following thermodynamic stability order (with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ in brackets in kJ mol^{-1}) amongst a selected group of sesquiterpenes [69]: β -cedrene (**70**) 47.1 [0.0] > α -cedrene (**64**) 48.9 [+1.8] > longifolene (**62**) 82.8 [+35.7] > β -caryophyllene (**48**) 161.0 [+113.9] > γ -gurjunene (**54**) 233.8 [+186.7]. In comparison, the G4/G4(MP2) order from the current work (with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ in brackets in kJ mol^{-1}) on the same compound suite is α -cedrene (**64**) [0.0/0.0] > β -cedrene (**70**) [+14.5/+14.5] > longifolene (**62**) [+40.2/+40.3] > γ -gurjunene (**54**) [+92.6/+90.7] > β -caryophyllene (**48**) [+169.7/+167.7]. Without the quantitative results, the rank orders are **70>64>62>48>54** for the prior work versus **64>70>62>54>48** for the current G4/G4(MP2) study.

Another study on the 0 K thermodynamic stability order (with $\Delta_{\text{isom}}H_{0\text{K},(\text{g})}$ in brackets in kJ mol^{-1}) at the B3LYP/6-31G* and MP2/6-31G** levels, respectively, for various sesquiterpenes reported the following order [70]: δ -selinene (**58**) [0.0/0.0] > δ -cadinene (**56**) [+23.9/+33.1] > α -muurolene (**44**) [+26.4/+32.9] > β -cadinene (**47**) [+28.2/+33.7] > α -cadinene (**40**) [+36.1/+42.7] > γ -muurolene (**55**) [+44.1/+46.2] > γ -cadinene (**53**) [+44.7/+49.3] > α -amorphene (**39**) [+53.0/+56.7] > α -copaene (**65**) [+85.6/+56.1] > ylangene (**63**) [+86.0/+55.1] > germacrene D (**26**) [+141.7/+175.6]. By contrast, the G4/G4(MP2) order from the current work (with $\Delta_{\text{isom}}H^\circ_{(\text{g})}$ in brackets in kJ mol^{-1}) for this group of compounds is δ -selinene (**58**) [0.0/0.0] > β -cadinene (**47**) [+22.6/+21.1] > α -muurolene (**44**) [+23.0/+22.1] > α -amorphene (**39**) [+23.0/+21.8] > δ -cadinene (**56**) [+26.1/+25.4] > α -cadinene (**40**) [+32.0/+30.5] > γ -muurolene (**55**) [+33.7/+33.0] > γ -cadinene (**53**) [+35.2/+33.8] > ylangene (**63**) [+59.2/+59.5] > α -copaene (**65**) [+60.1/+60.3] > germacrene D (**26**) [+143.0/+140.3]. Without the quantitative results, the rank orders are **58>56>44>47>40>55>53>39>65>63>26** for the prior work versus **58>47>44>39>56>40>55>53>63>65>26** for the current G4/G4(MP2) study.

Gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) adiabatic ionization energies ($\text{AIE}_{298\text{K}}$) and 0 K adiabatic ionization energies ($\text{AIE}_{0\text{K}}$) of the monoterpenes (compounds **1–20**) investigated in this work were also calculated at the G4 and G4(MP2) levels of theory (Table 4; all AIE values are positive). The calculated $\text{AIE}_{298\text{K}}$ and $\text{AIE}_{0\text{K}}$ values span the range 7.33/7.33–8.58/8.55 eV (G4/G4(MP2)) and 7.32/7.31–8.57/8.54 eV (G4/G4(MP2)), respectively, a consistent spread of 1.22–1.25 eV that reflects primarily the degree and substitution pattern of unsaturation within this isomeric $\text{C}_{10}\text{H}_{16}$ series.

The agreement between the two composite methods is uniformly excellent (Figure 5). The G4(MP2) values lie systematically below their G4 counterparts by only 0.01–0.05 eV (mean deviation $\approx$ 0.03 eV or 2.9 kJ mol^{-1}), and the rank ordering of the twenty compounds is preserved between the two methods for the $\text{AIE}_{298\text{K}}$ data. The relative ordering of β -myrcene (**16**) and α -pinene (**13**) is inverted between the 0 K and 298 K datasets, the two species being separated by only 0.01 eV at either temperature. This inversion arises not from a temperature-induced shift in the β -myrcene value, which is essentially unchanged between 0 K and 298 K, but from a slightly larger thermal correction to α -pinene (+0.02

eV). Differences of this magnitude lie within the two-decimal precision of the tabulated values and within the residual uncertainty of the G4 and G4(MP2) thermal corrections. The two compounds are accordingly regarded as energetically degenerate within the resolution of the present calculations, and no physical significance is attached to their ordering at either temperature.

A survey of the NIST Chemistry WebBook [51] identified experimental determinations for only four of the twenty monoterpenes examined here: α -pinene (**13**), 8.07 eV by photoelectron (PE) spectroscopy [71]; limonene (**3**), 8.3 eV by electron-impact (EI) ionization [72]; α -carene (**9**), 8.4 eV by PE spectroscopy [73]; and camphene (**2**), ≤ 8.86 eV as an upper bound by PE spectroscopy [74]. The primary literature adds to this picture. An electron-impact and UV-absorption study [75] reported AIEs of 8.3 eV for α -pinene (**13**) and 8.6 eV for β -pinene (**18**), which compared to the G3(MP2) calculated values of 8.29 eV and 8.41 eV, respectively. Other work has reported an AIE for α -pinene (**13**) of 8.16 eV using PE spectroscopy [76] and 8.15 eV using photoionization efficiency (PIE) spectra [77]. The AIE_{298K} obtained in the current work (8.17/8.14 eV (G4/G4(MP2))) is in excellent agreement with these latter two studies, and suggests that the historical reports of 8.07 eV and 8.3 eV bracket the true AIE_{298K} value of $\sim 8.16 \pm 0.01$ eV.

Further work on β -pinene (**18**) found an AIE of 8.60 eV using EI ionization and 8.45 ± 0.03 eV derived from the efficiency spectrum, the latter in good agreement with G3(MP2) (8.41 eV) and CBS-QB3 (8.38 eV) calculations [78]. A PIE spectra derived AIE of 8.45 eV [77] and PE spectroscopy derived insights also agree on 8.45 eV [76]. The G4/G4(MP2) estimates of 8.34/8.31 eV are significantly lower than all experimental reports, but in reasonable agreement with prior G3(MP2) (8.29 and 8.41 eV) and CBS-QB3 (8.38 eV) calculations, suggesting the actual AIE_{298K} of β -pinene (**18**) is likely 8.33 ± 0.04 eV.

Prior experimental measurements for the AIE of limonene (**3**) at 8.3 eV using EI ionization [72] and 8.27 eV derived from the photoionization efficiency spectrum (compared to a B3LYP/6-311++G calculated value of 8.08 eV) [79] are both likely too low. He(I) photoelectron spectroscopy has indicated an AIE of 8.521 ± 0.002 eV [80], supported by a PE spectroscopy report of 8.505 eV [76], 8.54 eV by atmospheric pressure photoionization (APPI) [81], and a ROVGF/cc-pVDZ//B3LYP/6-31G** calculation of 8.51 eV [82]. The G4/G4(MP2) AIE_{298K} of 8.58/8.55 eV reside within 0.01–0.06 eV of the He(I) photoelectron spectroscopy and APPI experimental reports, placing the most probable actual AIE_{298K} of limonene (**3**) at 8.55 ± 0.03 eV.

For α -carene (**9**), experimental values are consistent, with reports of 8.4 eV [73], 8.38 [76], and 8.385 [83] by PE spectroscopy. These values are in good agreement with the G4/G4(MP2) AIE_{298K} of 8.35/8.32 eV. Sabinene (**4**) has an inferred experimental AIE of 8 eV by PE spectroscopy [76], in excellent agreement with the G4/G4(MP2) estimate of 8.00/7.97 eV. α -Terpinene's (**14**) experimental PE spectroscopy AIE of 7.55 eV is also in excellent agreement with the G4/G4(MP2) calculations (7.56/7.53 eV) [84].

Finally, we note that the temperature dependence of the AIE is effectively negligible (0.00–0.03 eV; 2.9 kJ mol⁻¹) and within the calculation errors of each method. Not only is it of little consequence at the resolution achievable in most experiments, this distinction is also not relevant when computed values are to serve as reference standards for atmospheric chemistry applications, where ionization at ambient temperature is the quantity of interest.

For the monoterpenes, the wide variance in AIE across these structural isomers is primarily governed by the ability of the molecular framework to stabilize the resulting radical cation hole through π -conjugation, hyperconjugation, and σ - π orbital interactions. The most significant stabilizing effect on the radical cation, corresponding to the lowest ionization energies, arises from extended π -conjugation. Trans,trans- α -alloocimene (**7**), an acyclic fully conjugated triene, exhibits the lowest AIE in the dataset (7.33 eV at both the G4 and G4(MP2) levels). The extended delocalization of the electron hole across the conjugated triene system significantly lowers the energy penalty for electron removal relative to simpler dienes or isolated alkenes.

Among the cyclic systems, highly substituted conjugated dienes dominate the lowest AIE ranks. For example, α -terpinene (**14**; 7.56/7.53 eV; G4/G4(MP2)) and α -phellandrene (**12**; 7.86/7.85 eV; G4/G4(MP2)) rank second and third, respectively. The energetic magnitude of this conjugative stabilization is most clearly illustrated by comparing structural isomers. While α -terpinene (**14**) features a conjugated diene moiety within its six-membered ring, its isomer γ -terpinene (**20**) contains two isolated, non-conjugated double bonds. This structural restriction prevents extensive charge delocalization in the radical cation of **20**, resulting in a substantial energetic penalty of 0.72/0.71 eV (AIE_{298K}=8.28/8.24 eV; G4/G4(MP2)) compared to its conjugated counterpart.

Beyond traditional π - π conjugation, the data reveals that interactions between alkenes and highly strained fused ring systems can significantly lower ionization energies. Cyclopropane rings possess high p-character "Walsh orbitals" [85] that can effectively delocalize adjacent positive charge, analogous to a standard π -system. This σ - π conjugation is evident in the thujene and sabinene families. Compounds such as α -thujene (**15**; 7.94/7.89 eV; G4/G4(MP2)), sabinene (**4**; 8.00/7.97 eV; G4/G4(MP2)), and β -thujene (**19**; 8.10/8.06 eV; G4/G4(MP2)) all feature a double bond directly adjacent to a fused three-membered ring. Despite lacking true diene conjugation, these molecules exhibit noticeably lower ionization energies than standard isolated alkenes. In contrast, bicyclic systems containing a fused cyclopropane ring that is isolated

from the π -system by saturated carbons, such as α -carene (**9**; 8.35/8.32 eV; G4/G4(MP2)), lack this stabilizing orbital overlap and consequently exhibit higher ionization energies.

In the absence of extensive conjugation or stabilizing ring interactions, ionization energy is dictated by the degree of alkyl substitution on the double bond via hyperconjugation. More highly substituted alkenes generate more stable radical cations. This trend is shown by the pinene isomers: α -pinene (**13**), possessing a trisubstituted endocyclic double bond, has a lower $\text{AIE}_{298\text{K}}$ (8.17/8.14 eV; G4/G4(MP2)) than β -pinene (**18**; 8.34/8.31 eV; G4/G4(MP2)), which features a less substituted, disubstituted exocyclic double bond.

Tricyclene (**8**, 8.34/8.29 eV; G4/G4(MP2)) merits separate comment as the only fully saturated member of the series. Whereas unstrained saturated hydrocarbons typically exhibit first ionization energies in excess of 9 eV (e.g., $\text{AIE}_{298\text{K}}$ of *n*-decane (9.65 eV [51]), adamantane, 9.25 $\pm$ 0.04 eV [51], and *exo*-tricyclo[5.2.1.0^{2,6}]decane [JP-10], 9.35 $\pm$ 0.05 eV [86]), tricyclene ionizes more readily than six of the nineteen unsaturated monoterpenes examined, including its π -bearing bornane-skeleton congener camphene (**2**, 8.56/8.52 eV; G4/G4(MP2)), and lies $\sim$ 1 eV below the range expected for a saturated C₁₀ cage. This ease of ionization is attributed to σ -conjugation involving the Walsh orbitals of the fused cyclopropane ring, reinforced by hyperconjugation from the gem-dimethyl group and by relief of ring strain in the relaxed radical cation, which together render the strained σ framework a more effective electron donor than the isolated or unconjugated π bonds of the higher-AIE members.

The upper boundary of the ionization energy spectrum in this monoterpene dataset ($\text{AIE}_{298\text{K}} \geq 8.50/8.46$ eV; G4/G4(MP2)) is populated by molecules with fully isolated, poorly shielded π -systems. Compounds such as limonene (**3**; 8.58/8.54 eV; G4/G4(MP2)), α -fenchene (**10**; 8.58/8.54 eV; G4/G4(MP2)), camphene (**2**; 8.56/8.52 eV; G4/G4(MP2)), and bornylene (**1**; 8.50/8.46 eV; G4/G4(MP2)) represent the rigid, non-conjugated limits of the dataset. For these molecules, the energetic cost of localized ionization of a relatively isolated π -bond dictates the overall thermodynamic penalty, resulting in the highest barriers to electron ejection among the studied monoterpenes.

As with the monoterpenes, the G4 and G4(MP2) calculated $\text{AIE}_{298\text{K}}$ of the 54 sesquiterpene hydrocarbons examined here (compounds **21**–**74**) span a considerable window, from 7.21/7.15 eV for germacrene C (**25**; G4/G4(MP2)) to 8.57/8.49 eV for β -selinene (**52**), a range of 1.34–1.36 eV. Analogous to the findings for the monoterpenes discussed above, because ionization in these alkenes proceeds predominantly from the π manifold, the AIE effectively serves as a probe of the highest occupied molecular orbital energy, which is in turn modulated by the degree of alkyl substitution on the olefinic carbons, the presence or absence of conjugative coupling between double bonds, and conformational/geometric constraints imposed by the carbon skeleton.

From a methodological standpoint, the G4 and G4(MP2) datasets track one another closely, differing by 0.03–0.10 eV, with G4 uniformly returning the higher values. More importantly, the rank ordering is essentially preserved across the two protocols. The handful of inversions that do occur arise exclusively within near-degenerate pairs separated by ≤ 0.05 eV (i.e., within the expected uncertainty of either composite method). Similarly, the thermal correction connecting $\text{AIE}_{0\text{K}}$ and $\text{AIE}_{298\text{K}}$ is small and consistently positive (typically +0.01–0.02 eV, ranging from 0.00–0.04), reflecting the modest differential zero-point and thermal contributions between the neutral and cationic manifolds.

The lower boundary of the sesquiterpene's ionization-energy spectrum is populated exclusively by molecules capable of extensive stabilization of the cationic charge, particularly the germacrenes. Germacrene C (**25**) exhibits the lowest $\text{AIE}_{298\text{K}}$ at 7.21/7.15 eV (G4/G4(MP2)), maintaining this rank at 0 K. This stabilization arises from the disposition of three endocyclic, alkyl-substituted double bonds (two of which are conjugated) within the flexible ten-membered ring, permitting efficient hyperconjugative and – depending on the reactive conformer – through-space delocalization of the positive charge. Bicyclogermacrene (**35**) ranks second lowest (7.26/7.18 eV; G4/G4(MP2)), attributable to two endocyclic, alkyl-substituted double bonds (albeit unconjugated) and especially the interaction between the Walsh orbitals of its strained, ring-fused cyclopropane and the adjacent endocyclic π -system, which mimics a conjugated diene in its charge-stabilizing capacity. This allows the diene bicyclogermacrene (**35**) to behave as an effective conjugated diene endocyclic triene that has an AIE only marginally above a true conjugated diene endocyclic triene germacrene C (**25**), and significantly below the endocyclic diene unconjugated triene compounds germacrenes D (**26**), A (**23**), and B (**24**). Germacrene D (**26**, 7.47/7.40 eV; G4/G4(MP2)) retains a significantly lower $\text{AIE}_{298\text{K}}$ than germacrenes A (**23**, 7.65/7.58 eV; G4/G4(MP2)) and B (**24**, 7.69/7.62 eV; G4/G4(MP2)) because, unlike these other two isomers, there is endo-exo conjugation in **26** versus a lack of conjugation in **23** or **24** (whose AIEs are effectively equivalent with the computational margin of error).

The structural factors governing the sesquiterpene AIEs are also explicitly demonstrated by the selinene isomers, which span nearly the entirety of the dataset's range. δ -Selinene (**58**) contains a disubstituted conjugated endocyclic olefin within the eudesmane bicyclic framework, ranking among the lowest members with an $\text{AIE}_{298\text{K}}$ of 7.27/7.20 eV (G4/G4(MP2)). The fully internal character of the unsaturation provides maximal alkyl shielding and hyperconjugative support of the ionized state. Perturbing this arrangement shifts the $\text{AIE}_{298\text{K}}$ by $\sim$ 1.0 eV for α -selinene (**45**; 8.28/8.20 eV; G4/G4(MP2)), in which isolation of the two alkenes (one of which is now exocyclic) curtails any cooperative stabilization. β -Selinene (**52**) represents the dataset maximum at 8.57/8.49 eV (G4/G4(MP2)). Its two double bonds

are mutually isolated, both exocyclic, and geometrically confined within the rigid decalin framework, affording little opportunity for delocalization or relaxational stabilization of the radical cation, and demanding ~1.3 eV more energy for ionization than its δ -isomer.

The energetic penalty associated with poorly substituted olefins is independent of the specific molecular scaffold. Among the acyclic isomers, the 1,3-conjugated diene moiety with a 3-methyl substituted internal double bond in the tetrane α -farnesene (**21**) yields a moderate $\text{AIE}_{298\text{K}}$ of 7.82/7.76 eV (G4/G4(MP2)), whereas the isomeric tetrane β -farnesene (**22**), in which the conjugated diene only contains two terminal CH_2 units, requires 8.04/7.96 eV (G4/G4(MP2)). Additional conjugated alkene-cyclopropyl effects are seen with α -gurjunene (**67**, 7.31/7.23 eV; G4/G4(MP2)) and β -gurjunene (**73**, 8.05/7.96 eV; G4/G4(MP2)), as well as to a lesser extent for α -cubebene (**66**, 7.58/7.50 eV; G4/G4(MP2)) and β -cubebene (**72**, 7.71/7.63 eV; G4/G4(MP2)), respectively, whereby the shift from an exocyclic olefin unconjugated to the cyclopropyl functionality in **73** to the endocyclic alkene conjugated to the three-carbon ring in **67** lowers the $\text{AIE}_{298\text{K}}$ by 0.74/0.73 eV (G4/G4(MP2)), and converting the exocyclic conjugated cyclopropyl in **72** to the endocyclic conjugated cyclopropyl in **66** reduces the $\text{AIE}_{298\text{K}}$ by 0.13 eV at both levels of theory.

Taken together, the composite data indicate that the thermodynamic cost of sesquiterpene ionization is minimized by medium-ring flexibility coupled with heavily substituted, spatially proximate internal olefins and/or conjugated alkene-cyclopropyl moieties, and maximized by rigid polycyclic scaffolds bearing isolated, weakly substituted alkenes. The close mutual tracking of G4 and G4(MP2) across this broad AIE span, with a near-constant minimal offset and rank inversions confined to near-degenerate pairs, confirms that these structure-energy trends are robust with respect to the treatment of the correlation space.

4. Conclusions

High-level G4 and G4(MP2) composite calculations have provided a comprehensive, internally consistent set of gas-phase standard state enthalpies of formation ($\Delta_f H^\circ_{(\text{g})}$) and enthalpies of isomerization ($\Delta_{\text{isom}} H^\circ_{(\text{g})}$), as well as gas-phase standard state adiabatic ionization energies ($\text{AIE}_{298\text{K}}$) and 0 K adiabatic ionization energies ($\text{AIE}_{0\text{K}}$) for 74 atmospherically relevant monoterpene and sesquiterpene hydrocarbons. Where experimental data exist, the calculated $\Delta_f H^\circ_{(\text{g})}$ and $\Delta_{\text{isom}} H^\circ_{(\text{g})}$ agree within effective chemical accuracy. The G4 and G4(MP2) thermodynamic stability rankings reinforce several structure–stability principles. Acyclic trienes suffer a substantial penalty relative to their cyclic and polycyclic congeners. Cyclization confers stabilization that is modulated by ring strain, ring-fusion stereochemistry, and double-bond position and substitution. AIEs across both compound classes are controlled by the degree of π -conjugation, stabilizing alkene–cyclopropyl Walsh orbital interactions, and alkyl substitution on the olefinic carbons. Where reliable experimental $\text{AIE}_{298\text{K}}$ are available, the G4/G4(MP2) estimates reproduce them within expected combined uncertainties, and several historically discordant literature values can be reconciled in favor of the present calculations.

The mutual consistency of the G4 and G4MP2 protocols across rigid and flexible frameworks confirms that either method is suitable for extending this dataset to further terpenoid isomers. More broadly, the discrepancies observed with common group contribution and lower-level DFT approaches for these compound classes underscore the value of the present high-level composite benchmarks. By filling critical thermochemical data gaps for these structurally complex isomers, this dataset provides the reference standards necessary to refine atmospheric chemistry mechanisms. The resulting thermodynamic and electronic data should find direct application in improving structure–activity relationships for oxidant attack rates and secondary organic aerosol yield parameterizations involving biogenic monoterpenes and sesquiterpenes, thereby supporting more robust models of tropospheric oxidizing capacity and aerosol-driven climate regulation.

Declarations

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Competing Interests

The authors declare that they have no financial or non-financial interests that are directly or indirectly related to the work submitted for publication.

Authors' Contributions

All authors contributed equally to the study conception, design, and execution. Computational methodology, software validation, and quantum-chemical evaluations were performed by Sierra Rayne and Kaya Forest. Data curation, analysis, and visualization were conducted

jointly by all authors. The original draft was written by Sierra Rayne and Kaya Forest, and all authors read, reviewed, and approved the final manuscript.

Research Involving Human Participants and/or Animals

This article does not contain any studies involving human participants or animals performed by any of the authors.

Informed Consent

Not applicable.

Data Availability

The datasets generated and analyzed during the current study are available from the corresponding authors upon reasonable request.

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Tables

Table 1

Gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of formation ($\Delta_f H^\circ_{(g)}$) and gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of isomerization ($\Delta_{\text{isom}} H^\circ_{(g)}$) for the monoterpenes (compounds **1** through **20**) under consideration at the G4 and G4(MP2) levels of theory. Values are in kJ mol⁻¹. $\Delta_{\text{isom}} H^\circ_{(g)}$ are referenced to the lowest-enthalpy isomer at each level with thermodynamical stability rank shown in brackets.

ID	Common name	$\Delta_f H^\circ_{(g)}$ (kJ mol ⁻¹)		$\Delta_{\text{isom}} H^\circ_{(g)}$ (kJ mol ⁻¹)	
		G4	G4(MP2)	G4	G4(MP2)
8	tricyclene	-25.3	-25.5	0.0 [1]	+1.4 [3]
2	camphene	-25.0	-26.9	+0.3 [2]	0.0 [1]
10	α -fenchene	-23.9	-26.1	+1.3 [3]	+0.8 [2]
14	α -terpinene	-15.0	-17.9	+10.2 [4]	+9.1 [4]
1	bornylene	-13.7	-16.0	+11.6 [5]	+11.0 [5]
20	γ -terpinene	-8.6	-12.2	+16.7 [6]	+14.8 [6]
17	β -phellandrene	-3.3	-7.5	+21.9 [7]	+19.4 [7]
12	α -phellandrene	-1.6	-5.6	+23.7 [8]	+21.4 [8]
5	terpinolene	+1.1	-1.9	+26.3 [9]	+25.0 [9]
3	limonene	+1.9	-1.9	+27.2 [10]	+25.1 [10]
9	α -carene	+24.3	+22.6	+49.6 [11]	+49.6 [11]
13	α -pinene	+26.4	+24.3	+51.7 [12]	+51.2 [12]
15	α -thujene	+29.2	+27.9	+54.4 [13]	+54.8 [13]
19	β -thujene	+35.7	+34.1	+61.0 [14]	+61.0 [14]
4	sabinene	+35.9	+34.6	+61.2 [15]	+61.5 [16]
18	β -pinene	+36.7	+34.5	+62.0 [16]	+61.4 [15]
7	trans,trans-alloocimene	+43.9	+39.5	+69.2 [17]	+66.4 [17]
6	trans- β -ocimene	+76.5	+71.6	+101.8 [18]	+98.6 [18]
16	β -myrcene	+78.6	+73.4	+103.9 [19]	+100.3 [19]
11	α -ocimene	+79.8	+74.6	+105.1 [20]	+101.5 [20]

Table 2

Gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of formation ($\Delta_f H^\circ_{(g)}$) and gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of isomerization ($\Delta_{\text{isom}} H^\circ_{(g)}$) for the sesquiterpenes (compounds **21** through **74**) under consideration at the G4 and G4(MP2) levels of theory. Values are in kJ mol⁻¹. $\Delta_{\text{isom}} H^\circ_{(g)}$ are referenced to the lowest-enthalpy isomer at each level with thermodynamical stability rank shown in brackets.

ID	Common name	$\Delta_f H^\circ_{(g)}$ (kJ mol ⁻¹)		$\Delta_{\text{isom}} H^\circ_{(g)}$ (kJ mol ⁻¹)		ID	Common name	$\Delta_f H^\circ_{(g)}$ (kJ mol ⁻¹)		$\Delta_{\text{isom}} H^\circ_{(g)}$ (kJ mol ⁻¹)	
		G4	G4(MP2)	G4	G4(MP2)			G4	G4(MP2)	G4	G4(MP2)
74	β -patchoulene	-142.2	-143.4	0.0 [1]	0.0 [1]	72	β -cubebene	-40.1	-41.5	+102.1 [28]	+101.9 [29]
61	isolongifolene	-132.4	-133.4	+9.8 [2]	+10.1 [3]	54	γ -gurjunene	-39.6	-43.1	+102.6 [29]	+100.3 [27]
64	α -cedrene	-132.2	-133.8	+9.9 [3]	+9.6 [2]	36	thujopsene	-37.3	-38.5	+104.9 [30]	+104.9 [30]
70	β -cedrene	-117.8	-119.3	+24.4 [4]	+24.1 [4]	67	α -gurjunene	-36.9	-37.8	+105.3 [31]	+105.6 [31]
58	δ -selinene	-113.6	-116.1	+28.6 [5]	+27.3 [5]	69	β -bourbonene	-24.6	-26.4	+117.5 [32]	+117.1 [32]
62	longifolene	-92.0	-93.5	+50.2 [6]	+49.9 [9]	68	α -santalene	-24.6	-26.0	+117.6 [33]	+117.4 [33]
47	β -cadinene	-91.0	-95.0	+51.2 [7]	+48.4 [6]	51	β -santalene	-22.4	-25.7	+119.7 [34]	+117.7 [34]
44	α -muurolene	-90.6	-94.0	+51.6 [8]	+49.5 [8]	60	aromadendrene	-20.8	-22.8	+121.4 [35]	+120.7 [35]
39	α -amorphene	-90.6	-94.3	+51.6 [9]	+49.2 [7]	59	alloaromadendrene	-12.0	-13.3	+130.2 [36]	+130.1 [36]
56	δ -cadinene	-87.5	-90.7	+54.7 [10]	+52.7 [10]	31	β -sesquiphellandrene	-5.8	-11.2	+136.4 [37]	+132.3 [37]
40	α -cadinene	-81.6	-85.6	+60.6 [11]	+57.8 [11]	73	β -gurjunene	-5.6	-7.1	+136.6 [38]	+136.3 [40]
45	α -selinene	-81.2	-84.9	+61.0 [12]	+58.5 [12]	28	α -sesquiphellandrene	-4.1	-9.4	+138.1 [39]	+134.0 [38]
55	γ -muurolene	-79.9	-83.1	+62.3 [13]	+60.4 [13]	32	γ -bisabolene	-3.4	-7.5	+138.8 [40]	+136.0 [39]
53	γ -cadinene	-78.4	-82.3	+63.8 [14]	+61.1 [14]	34	δ -elemene	+1.0	-3.6	+143.1 [41]	+139.9 [41]
52	β -selinene	-77.8	-81.4	+64.4 [15]	+62.0 [15]	29	β -bisabolene	+2.0	-2.7	+144.2 [42]	+140.7 [42]
41	α -chamigrene	-75.8	-79.2	+66.4 [16]	+64.2 [16]	27	α -bisabolene	+4.1	-0.7	+146.2 [43]	+142.7 [43]
43	α -himachalene	-65.9	-69.0	+76.3 [17]	+74.4 [17]	33	γ -elemene	+13.8	+9.5	+156.0 [44]	+153.0 [44]
50	β -himachalene	-65.1	-68.2	+77.1 [18]	+75.2 [18]	30	β -elemene	+14.9	+9.7	+157.1 [45]	+153.2 [45]
46	β -alaskene	-64.7	-67.9	+77.5 [19]	+75.5 [19]	25	germacrene C	+22.0	+16.6	+164.2 [46]	+160.0 [46]
49	β -guaiene	-56.7	-59.3	+85.5 [20]	+84.1 [20]	24	germacrene B	+28.2	+22.9	+170.4 [47]	+166.4 [47]
38	α -alaskene	-55.7	-59.1	+86.5 [21]	+84.3 [21]	26	germacrene D	+29.4	+24.2	+171.6 [48]	+167.7 [48]
42	α -guaiene	-55.2	-58.3	+86.9 [22]	+85.1 [22]	48	β -caryophyllene	+37.5	+33.9	+179.7 [49]	+177.3 [49]
63	ylangene	-54.4	-56.6	+87.8 [23]	+86.8 [23]	37	trans- β -bergamotene	+39.0	+35.4	+181.2 [50]	+178.8 [51]
65	α -copaene	-53.5	-55.8	+88.7 [24]	+87.7 [24]	23	germacrene A	+39.5	+34.0	+181.7 [51]	+177.4 [50]

57	δ -guaiene	-52.0	-55.3	+90.2 [25]	+88.2 [25]	35	bicyclogermacrene	+44.3	+40.7	+186.5 [52]	+184.2 [52]
66	α -cubebene	-47.3	-48.8	+94.8 [26]	+94.7 [26]	21	α -farnesene	+76.6	+70.2	+218.8 [53]	+213.6 [53]
71	β -copaene	-40.7	-42.6	+101.5 [27]	+100.8 [28]	22	β -farnesene	+80.4	+73.7	+222.6 [54]	+217.2 [54]

Table 3

Comparison between derived experimental gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of formation ($\Delta_f H^\circ_{(g),der}$) obtained from the addition of the liquid-phase standard state (298.15 K) enthalpies of formation ($\Delta_f H^\circ_{(l)}$) and the standard state (298.15 K) enthalpies of vaporization ($\Delta_{vap} H^\circ$) and the corresponding calculated $\Delta_f H^\circ_{(g)}$ at the G4 and G4(MP2) levels of theory. Values are in kJ mol⁻¹.

Experimental						
ID	Common name	$\Delta_f H^\circ_{(l)}$ (kJ mol ⁻¹) [51]	$\Delta_{vap} H^\circ$ (kJ mol ⁻¹) [51]	$\Delta_f H^\circ_{(g),der}$ (kJ mol ⁻¹) ^g	G4	G4(MP2)
3	limonene	-50.5±4.0 [87–89] ^a	+49.5±0.5 ^b	-1.0±2.5	+1.9	-1.9
9	α -carene	-29.5 [53, 87]	+48.4±3.1 ^c	+18.9±3.7	+24.3	+22.6
13	α -pinene	-16.4 [87, 88]	+44.6±0.3 ^d	+28.2±3.0	+26.4	+24.3
16	β -myrcene	+14.5 [87, 88]	+50.6±2.0 ^e	+65.1±3.0 (or ≥±10)	+78.6	+73.4
18	β -pinene	-7.7 [87, 88]	+45.8±0.3 ^f	+38.1±3.0	+36.7	+34.5

^a Adopted as the mean of two determinations: -54.5 kJ mol⁻¹ [87, 88] and -46.5 kJ mol⁻¹ [89].

^b Adopted as the mean of six mutually consistent determinations: direct calorimetric measurement of +48.9±0.1 kJ mol⁻¹ [90], vapor-pressure-derived standard-state values of +49.6±0.2 and +49.5 kJ mol⁻¹ [89, 91], and GC/CGC retention-correlation determinations of +49.6 kJ mol⁻¹ [92], +49.9 kJ mol⁻¹ [93] and +49.6 kJ mol⁻¹ [94]. All five values agree within 1.0 kJ mol⁻¹; the operative uncertainty of ±0.5 kJ mol⁻¹ conservatively reflects this spread plus the heat-capacity-dependent conventions of the compiler adjustments (AC). Earlier literature values derived from early Antoine-coefficient reductions (≈+45.9 kJ mol⁻¹ at 302 K [95]) were excluded as outliers inconsistent with this five-fold consensus.

^c Adopted as the mean of two independent NIST Chemistry WebBook [51] evaluations of the determination of ref. [53] (+48.3±3.1 kJ mol⁻¹, ALS compilation; +48.5 kJ mol⁻¹, DRB compilation), both referring to the same underlying vapor-pressure measurements reported at standard conditions; no temperature extrapolation was required. The substantial assigned uncertainty (±3.1 kJ mol⁻¹, ≈6%) reflects the age and single-source nature of this determination, which appears to be the only direct measurement of the vaporization enthalpy of this compound in the compilation record.

^d Adopted from direct calorimetric determination [96]; consistent with the independent vapor-pressure-derived values (+45.4 kJ mol⁻¹ at standard conditions [91] and +45.0 kJ mol⁻¹ at 307 K [95]) and bracketed by +46.6 kJ mol⁻¹ at 288 K [97] and +43.4 kJ mol⁻¹ at 308 K [98]. The four independent vapor-pressure-derived estimates mutually agree within ~1.5 kJ mol⁻¹ despite spanning methods and decades, supporting adoption of the calorimetric value.

^e Adopted from the gas-chromatographic correlation determination [93] quoted by NIST Chemistry WebBook [51] at standard conditions. An older vapor-pressure-derived value (+45.7 kJ mol⁻¹ at 302 K, from Antoine-coefficient reductions of the compilation of ref. [95]) was judged less reliable and retained only as a lower bound: it derives from early bulk vapor-pressure data for this air-sensitive triene, whose handling history parallels that of the suspect 1954 combustion sample. No direct calorimetric determination of $\Delta_{vap} H^\circ$ appears to exist for this compound in the compilation record; the ~5 kJ mol⁻¹ spread between the two available sources is reflected in the operative uncertainty (±2 kJ mol⁻¹ adopted, a compromise recognizing that the GC-correlation method itself carries systematic uncertainty of this order, while acknowledging the directionality of the suspected bias in the older datum).

^f Adopted from the direct calorimetric determination of ref. [96] (vaporization calorimeter, quoted at standard conditions). Independent vapor-pressure-derived determinations corroborate this value within expected extrapolation error: +43.5 kJ mol⁻¹ at 288 K [97] (V method; tabulation

covers the α -/ β -pinene pair simultaneously) and +42.5 kJ mol⁻¹ at 335 K [99] (from VLE data over 320–429 K), which adjust to $\approx$ +46–47 and $\approx$ +45 kJ mol⁻¹ at 298.15 K respectively under a Watson-type temperature dependence, mutually consistent with the calorimetric value. No other near-ambient direct measurement of comparable quality exists for this compound.

⁹ Derived gas-phase enthalpies of formation were constructed as $\Delta_f H^\circ_{(g)} = \Delta_f H^\circ_{(l)} + \Delta_{\text{vap}} H^\circ_{298.15\text{K}}$, with $\Delta_f H^\circ_{(l)}$ values taken from oxygen-bomb combustion calorimetry as compiled and reanalyzed in the NIST Chemistry WebBook [51] and $\Delta_{\text{vap}} H^\circ_{298.15\text{K}}$ values from the sources cited in the table (direct calorimetry where available; otherwise gas-chromatographic correlation or vapor-pressure extrapolation, as noted per compound). Reported uncertainties represent 1 σ estimates obtained by quadrature propagation of three independent contributions: (i) the uncertainty of the condensed-phase formation enthalpy, as quoted from the original measurement or its subsequent reanalysis, whichever is larger; (ii) the uncertainty of the enthalpy of vaporization at 298.15 K, including, where applicable, an allowance of $\sim$ 1 kJ mol⁻¹ for extrapolation from measured temperatures to 298.15 K; and (iii) a nominal allowance of 0.5 kJ mol⁻¹ covering the convention-dependent corrections neglected in the simple (non-Washburn-corrected) reduction of combustion data. For β -myrcene, an additional sample-integrity caveat applies: the 1954 combustion determination [88] may be biased by degradation of the autoxidizable triene, and the effective uncertainty should be regarded as substantially larger ($\geq \pm 10$ kJ mol⁻¹) than the formal propagated value.

Table 4
Gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) adiabatic ionization energies (AIE_{298K}) and 0 K adiabatic ionization energies (AIE_{0K}) for the monoterpenes (compounds **1** through **20**) under consideration at the G4 and G4(MP2) levels of theory. Values are in eV with rank shown in brackets.

ID	Common name	AIE _{298K} (eV)		AIE _{0K} (eV)	
		G4	G4(MP2)	G4	G4(MP2)
7	trans,trans-alloocimene	7.33 [1]	7.33 [1]	7.32 [1]	7.31 [1]
14	α -terpinene	7.56 [2]	7.53 [2]	7.55 [2]	7.52 [2]
12	α -phellandrene	7.86 [3]	7.85 [3]	7.85 [3]	7.83 [3]
15	α -thujene	7.94 [4]	7.89 [4]	7.92 [4]	7.87 [4]
6	trans- β -ocimene	7.96 [5]	7.95 [5]	7.96 [5]	7.95 [5]
4	sabinene	8.00 [6]	7.97 [6]	7.98 [6]	7.95 [6]
5	terpinolene	8.05 [7]	8.00 [7]	8.04 [7]	7.99 [7]
19	β -thujene	8.10 [8]	8.06 [8]	8.08 [8]	8.05 [8]
11	α -ocimene	8.14 [9]	8.12 [9]	8.14 [9]	8.12 [9]
16	β -myrcene	8.16 [10]	8.13 [10]	8.16 [11]	8.13 [11]
13	α -pinene	8.17 [11]	8.14 [11]	8.15 [10]	8.12 [10]
17	β -phellandrene	8.21 [12]	8.19 [12]	8.20 [12]	8.18 [12]
20	γ -terpinene	8.28 [13]	8.24 [13]	8.27 [13]	8.22 [13]
8	tricyclene	8.34 [14]	8.29 [14]	8.34 [15]	8.28 [14]
18	β -pinene	8.34 [15]	8.31 [15]	8.31 [14]	8.28 [15]
9	α -carene	8.35 [16]	8.32 [16]	8.34 [16]	8.30 [16]
1	bornylene	8.50 [17]	8.46 [17]	8.48 [17]	8.45 [17]
2	camphene	8.56 [18]	8.52 [18]	8.54 [18]	8.51 [18]
10	α -fenchene	8.58 [19]	8.54 [19]	8.56 [19]	8.53 [19]
3	limonene	8.58 [20]	8.55 [20]	8.57 [20]	8.54 [20]

Table 5

Gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) adiabatic ionization energies ($AI E_{298K}$), and 0 K adiabatic ionization energies ($AI E_{0K}$) for the sesquiterpenes (compounds **21** through **74**) under consideration at the G4 and G4(MP2) levels of theory. Values are in eV with rank shown in brackets.

		AIE _{298K} (eV)		AIE _{0K} (eV)				AIE _{298K} (eV)		AIE _{0K} (eV)	
ID	Common name	G4	G4(MP2)	G4	G4(MP2)	ID	Common name	G4	G4(MP2)	G4	G4(MP2)
25	germacrene C	7.21 [1]	7.15 [1]	7.21 [1]	7.15 [1]	22	β-farnesene	8.04 [28]	7.96 [28]	8.04 [29]	7.96 [29]
35	bicyclogermacrene	7.26 [2]	7.18 [2]	7.25 [2]	7.16 [2]	39	α-amorphene	8.04 [29]	7.97 [30]	8.03 [28]	7.96 [30]
58	δ-selinene	7.27 [3]	7.20 [3]	7.26 [3]	7.19 [3]	73	β-gurjunene	8.05 [30]	7.96 [29]	8.04 [30]	7.95 [28]
67	α-gurjunene	7.31 [4]	7.23 [4]	7.30 [4]	7.21 [4]	31	β-sesquiphellandrene	8.06 [31]	8.01 [35]	8.05 [31]	8.01 [37]
49	β-guaiene	7.46 [5]	7.39 [5]	7.45 [5]	7.39 [5]	44	α-muurolene	8.07 [32]	7.99 [31]	8.06 [33]	7.98 [32]
26	germacrene D	7.47 [6]	7.40 [6]	7.47 [6]	7.39 [6]	71	β-copaene	8.07 [33]	7.99 [32]	8.05 [32]	7.97 [31]
66	α-cubebene	7.58 [7]	7.50 [7]	7.56 [7]	7.48 [7]	48	β-caryophyllene	8.08 [34]	8.00 [33]	8.07 [34]	8.00 [34]
23	germacrene A	7.65 [8]	7.58 [8]	7.64 [8]	7.57 [8]	60	aromadendrene	8.09 [35]	8.00 [34]	8.07 [35]	7.98 [33]
28	α-sesquiphellandrene	7.69 [9]	7.62 [9]	7.68 [9]	7.61 [9]	64	α-cedrene	8.10 [36]	8.02 [36]	8.08 [36]	8.00 [35]
24	germacrene B	7.69 [10]	7.62 [10]	7.68 [10]	7.61 [10]	59	alloaromadendrene	8.10 [37]	8.02 [37]	8.09 [37]	8.00 [36]
74	β-patchoulene	7.70 [11]	7.62 [11]	7.68 [11]	7.61 [11]	41	α-chamigrene	8.11 [38]	8.02 [38]	8.11 [38]	8.01 [38]
72	β-cubebene	7.71 [12]	7.63 [12]	7.69 [12]	7.62 [12]	37	trans-β-bergamotene	8.14 [39]	8.04 [39]	8.13 [39]	8.03 [39]
50	β-himachalene	7.72 [13]	7.63 [13]	7.70 [13]	7.62 [13]	68	α-santalene	8.16 [40]	8.06 [40]	8.14 [40]	8.04 [40]
32	γ-bisabolene	7.76 [14]	7.66 [14]	7.75 [14]	7.66 [14]	34	δ-elemene	8.18 [41]	8.08 [41]	8.17 [41]	8.07 [41]
38	α-alaskene	7.77 [15]	7.68 [15]	7.75 [15]	7.67 [15]	29	β-bisabolene	8.18 [42]	8.08 [42]	8.17 [42]	8.07 [42]
42	α-guaiene	7.77 [16]	7.68 [16]	7.76 [16]	7.67 [16]	69	β-bourbonene	8.20 [43]	8.13 [45]	8.18 [43]	8.11 [44]
57	δ-guaiene	7.80 [17]	7.72 [17]	7.79 [17]	7.71 [17]	55	γ-muurolene	8.21 [44]	8.12 [43]	8.20 [45]	8.11 [45]
21	α-farnesene	7.82 [18]	7.76 [18]	7.81 [18]	7.75 [18]	51	β-santalene	8.21 [45]	8.12 [44]	8.19 [44]	8.10 [43]
46	β-alaskene	7.86 [19]	7.78 [20]	7.85 [20]	7.77 [21]	43	α-himachalene	8.25 [46]	8.17 [46]	8.23 [46]	8.15 [46]
33	γ-elemene	7.86 [20]	7.78 [21]	7.86 [22]	7.77 [22]	53	γ-cadinene	8.27 [47]	8.18 [47]	8.26 [47]	8.17 [47]
36	thujopsene	7.87 [21]	7.78 [22]	7.84 [19]	7.76 [19]	45	α-selinene	8.28 [48]	8.20 [48]	8.26 [48]	8.18 [48]
56	δ-cadinene	7.87 [22]	7.77 [19]	7.85 [21]	7.76 [20]	62	longifolene	8.28 [49]	8.20 [49]	8.26 [49]	8.19 [50]
27	α-bisabolene	7.93 [23]	7.86 [23]	7.92 [23]	7.85 [24]	40	α-cadinene	8.29 [50]	8.20 [50]	8.28 [50]	8.18 [49]
65	α-copaene	7.93 [24]	7.86 [24]	7.92 [24]	7.84 [23]	47	β-cadinene	8.30 [51]	8.20 [51]	8.28 [51]	8.19 [51]
63	ylangene	7.96 [25]	7.88 [25]	7.94 [25]	7.86 [25]	70	β-cedrene	8.49 [52]	8.41 [52]	8.47 [52]	8.39 [52]

61	isolongifolene	7.96 [26]	7.88 [26]	7.95 [26]	7.86 [26]	30	β -elemene	8.55 [53]	8.46 [53]	8.54 [54]	8.45 [53]
54	γ -gurjunene	8.01 [27]	7.94 [27]	8.01 [27]	7.94 [27]	52	β -selinene	8.57 [54]	8.49 [54]	8.53 [53]	8.45 [54]

Figures

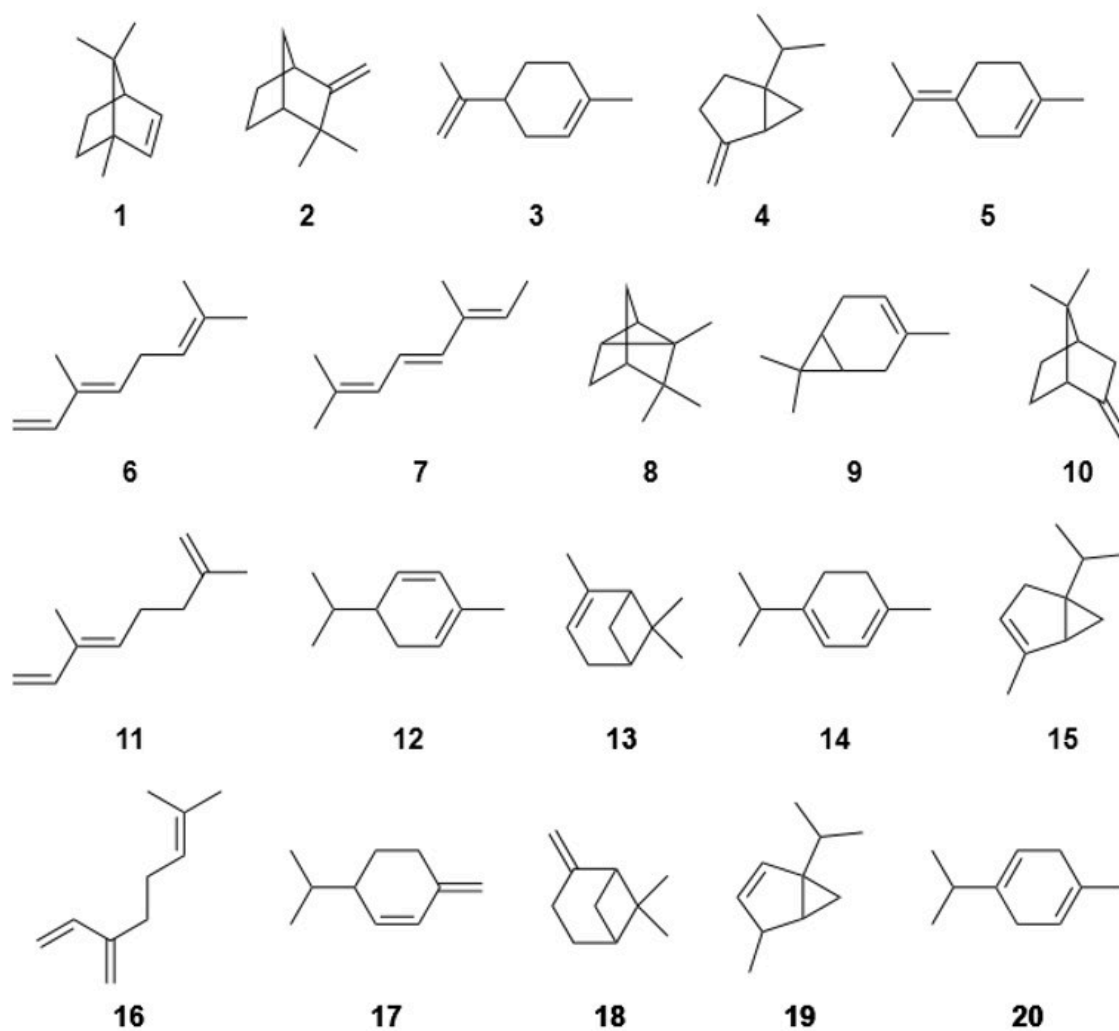


Fig. 1.

Figure 1

Structures of the monoterpenes (compounds **1** through **20**) under consideration.

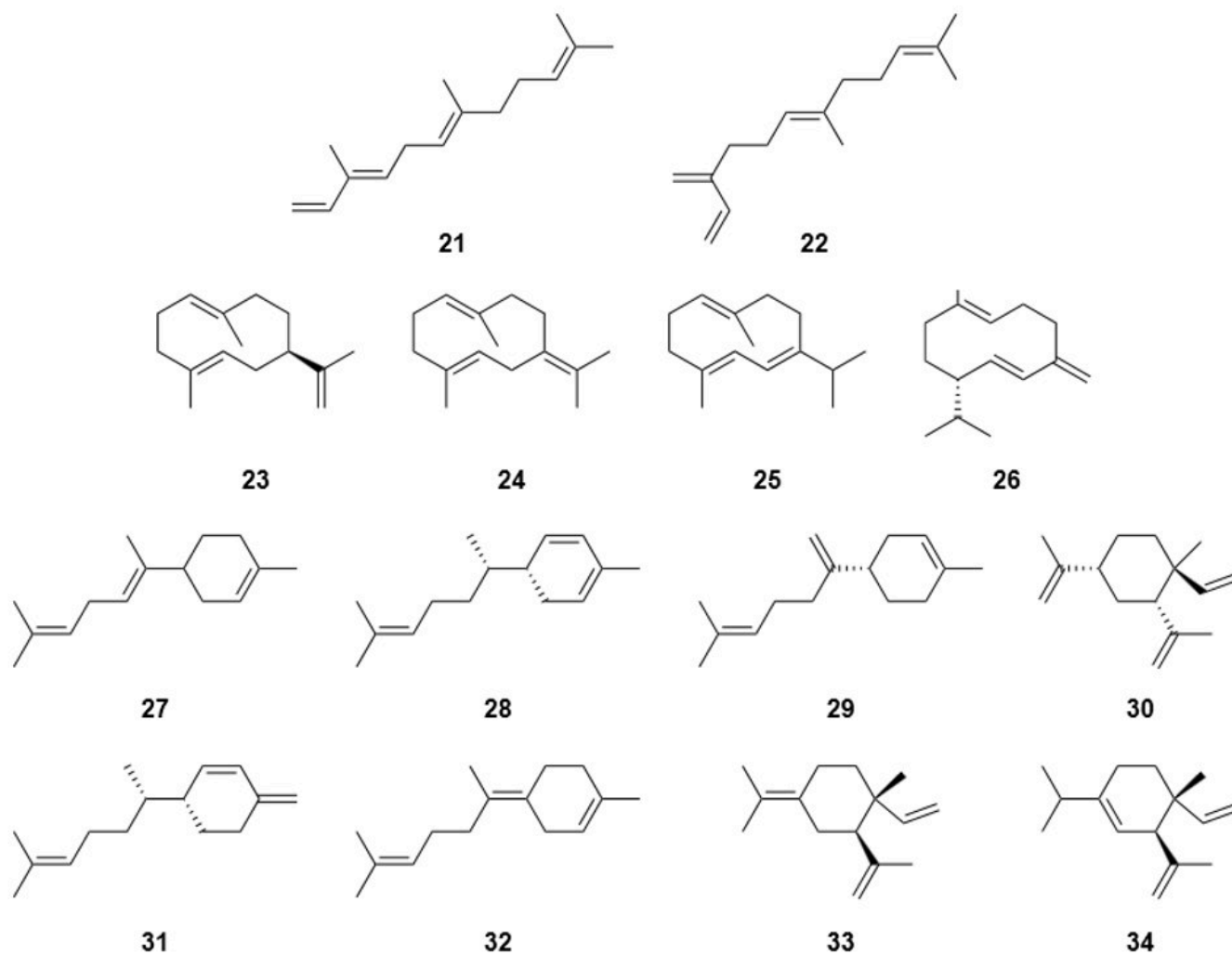


Fig. 2.

Figure 2

Structures of the acyclic (compounds **21** and **22**) and monocyclic (compounds **23** through **34**) sesquiterpenes under consideration.

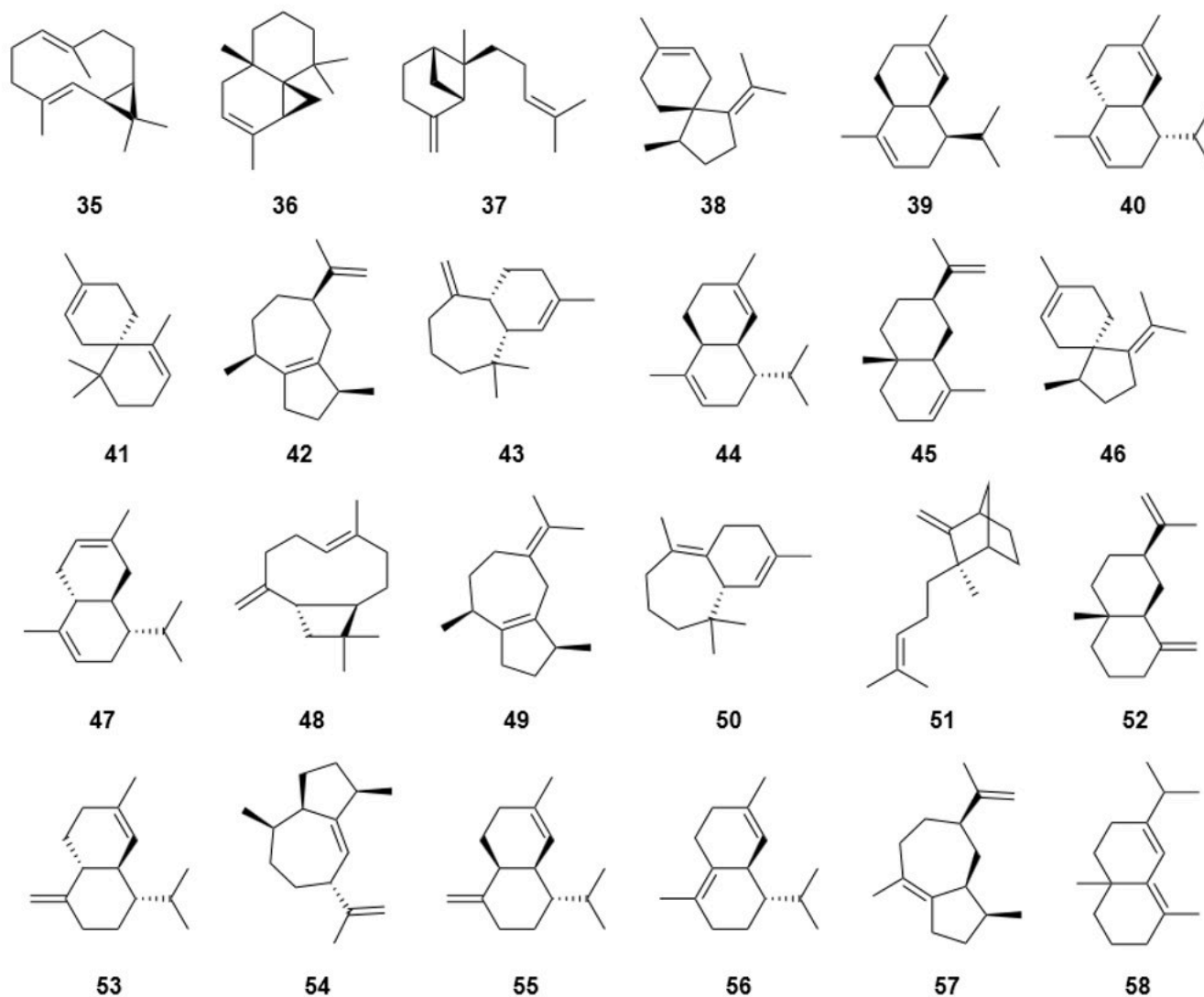


Fig. 3.

Figure 3

Structures of the bicyclic sesquiterpenes (compounds **35** through **58**) under consideration.

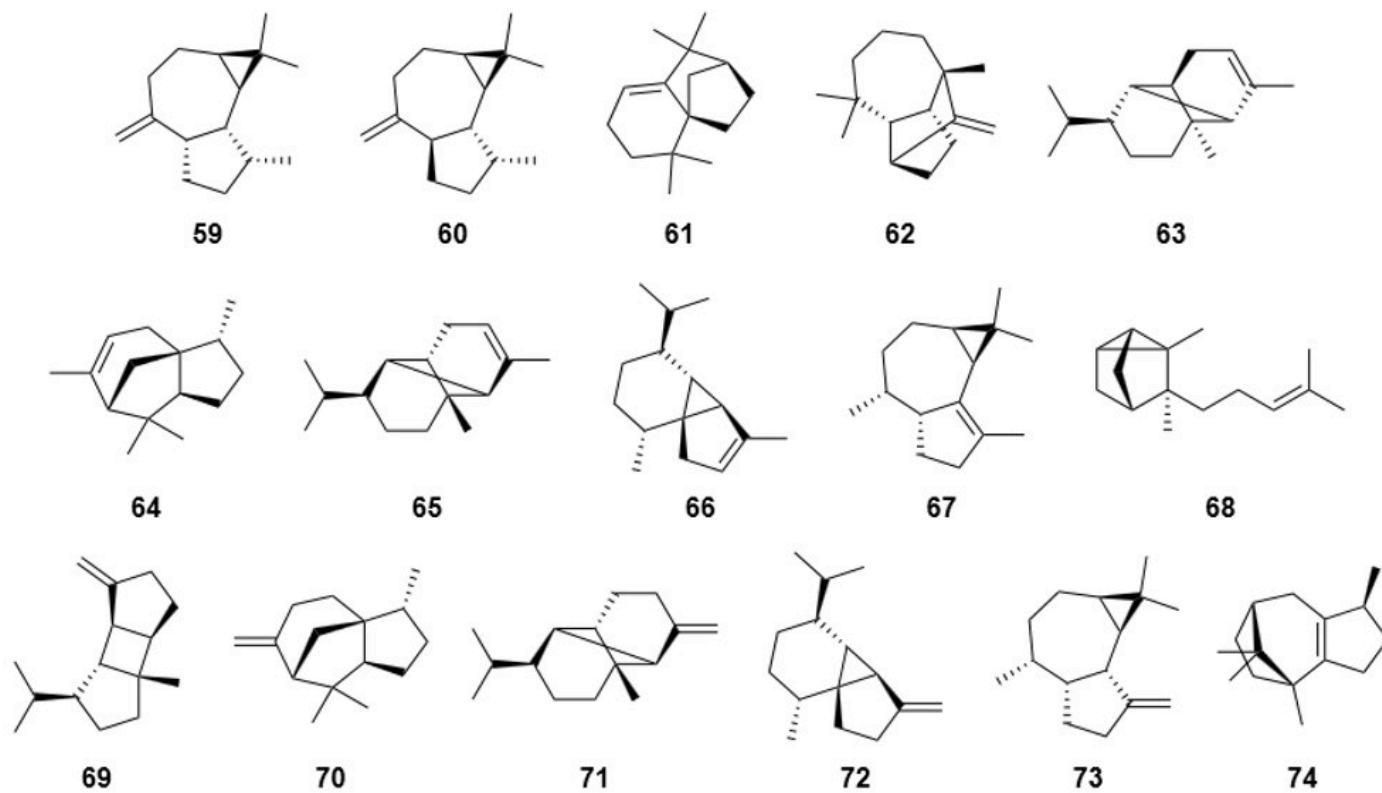


Fig. 4.

Figure 4

Structures of the tricyclic sesquiterpenes (compounds **59** through **74**) under consideration.

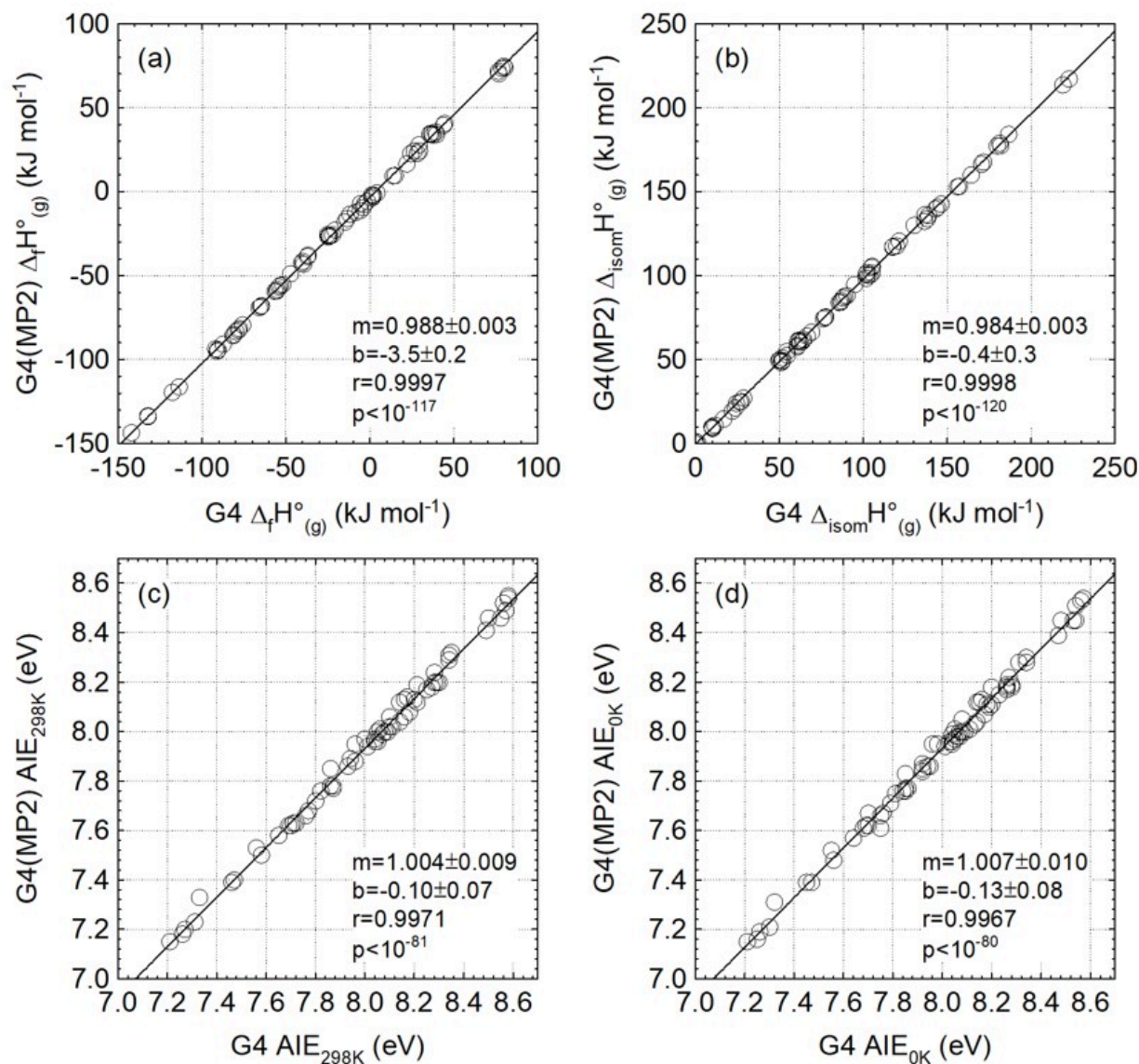


Fig. 5.

Figure 5

Correlations between G4 and G4(MP2) (a) gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of formation ($\Delta_f H^\circ_{(g)}$), (b) gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of isomerization ($\Delta_{isom} H^\circ_{(g)}$), (c) gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) adiabatic ionization energies (AIE_{298K}), and (d) 0 K adiabatic ionization energies (AIE_{0K}) for the monoterpenes (compounds **1** through **20**) and sesquiterpenes (compounds **21** through **74**) under consideration. Linear regression statistics are provided as insets in each plot. Error bars on regression statistics are standard errors.