Supporting Information

Thermodynamics of the Isomerization of Monoterpene Epoxides

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CONTENT

1. Group Contribution Methods for calculating thermodynamic properties

1.1. Benson (B)
1.2. Joback-Reid (JR)
1.3. Constantinou-Gani (CG)
1.4. Ghasemitabar-Movagharnejad (GM)
1.5. Tahami-Movagharnejad-Ghasemitabar (TMG)
1.6. Abdi-Movagharnejad-Ghasemitabar (AMG)

LIST OF FIGURES

Figure S1. Tendencies of enthalpy and Gibbs free energy of reaction as a function of reciprocal of dielectric constant for a) \(\alpha\)-pinene epoxide isomers and b) \(\beta\)-pinene epoxide isomers.
1. Group Contribution Methods for calculating thermodynamic properties

1.1. Benson method (B)

The Benson method is the most used group contribution methodology to estimate thermodynamic properties of organic compounds. Benson et al. developed a technique for estimating the standard enthalpy of formation \( \Delta H_f^{\circ},298 \) in gas phase Eq. (S1). The principle of its procedure is to calculate the properties by the partial addition of group contributions \( n_k \) composing molecules whose values are found in the literature [1]. The contribution of each group \( k \) in the standard enthalpy of formation is given by \( H_f^{\circ},298_k \).

\[
H_f^{\circ},298 = \sum_k n_k H_f^{\circ},298_k
\]

(S1)

In this method the group is expressed as E-(A)\(_x\)(B)\(_y\)(C)\(_z\), where E is the central atom, typically C, C\(_{\text{dbl}}\) (sp\(^2\) or double bond carbon) or O. The elements (A, B, C) correspond to groups which are bound to the central atom, and the subscripts \( x, y \) and \( z \) refer to the amount of the respective atom bonded.

1.2. Joback-Reid method (JR)
The Joback-Reid is a group contribution method for the estimation of physical properties of pure compounds (normal boiling point \( T_b \), normal freezing point \( T_f \), critical pressure \( P_c \), critical temperature \( T_c \), critical volume \( V_c \), ideal gas enthalpy of formation \( \Delta H_{o,298}^f \), ideal gas Gibbs energy of formation \( \Delta G_{o,298}^f \), ideal gas heat capacities \( \Delta C^o_p \), normal enthalpy of vaporization \( \Delta H_{vb} \), and enthalpy of fusion \( \Delta H_f \)), by Eq. (S2) to Eq. (S11). It uses a common set of structural groups. High accuracy is not claimed, but the methods is often as accurate as or more accurate than other techniques in common use.

\[
T_b = 198.2 + \sum \\
T_f = 122.5 + \sum \\
T_c = T_b \left[ 0.584 + 0.965 \sum - \left( \sum \right)^2 \right]^{-1} \\
P_c = \left( 0.113 + 0.0032n_A - \sum \right)^{-2} \\
V_c = 17.5 + \sum \\
\Delta H_{o,298}^f = 68.29 + \sum \\
\Delta G_{o,298}^f = 53.88 + \sum \\
\Delta C^o_p = \sum (a) - 37.93 + [\sum (b) + 0.210]T + [\sum (c) - 3.91 \times 10^{-4}]T^2 \\
\quad + [\sum (d) + 2.06 \times 10^{-7}]T^3 \\
\Delta H_{vb} = 15.30 + \sum \\
\Delta H_f = -0.88 + \sum
\]

The notation \( \sum \) indicates that, for the particular property of interest, one sums the product of the number of times a group appears in the compound and the group contributions [2].

1.3. Constantinou-Gani method (CG)
Constantinou and Gani developed a group contribution method for the estimation of properties of pure organic compounds. In this method the estimation comprises two levels of contributions: the basic level uses contribution for first-order groups $i$ and in the second level a small set of second-order group contributions $j$ are introduced. The methodology is useful in the estimation of normal boiling point $T_b$, critical properties (temperature $T_c$, pressure $P_c$, and volume $V_c$), normal melting point $T_m$, standard enthalpy of vaporization at 298 K $\Delta H_v$, standard Gibbs energy $\Delta G_f$ and standard enthalpy of formation at 298 K $\Delta H_f$, by Eq. (S12) to Eq. (S19).

The first and second order group contributions data and the values of the additional adjustable parameters in the equations are presented in the main reference of the method [3]. Table S1 shows an application example of the method in the estimation of pinocarveol properties.

Table S1. Example of Pinocarveol properties estimation by Constantinou-Gani method.
### Pinocarveol

| t_{ci} | p_{ci} (bar^{0.5}) | v_{ci} (m^{3}/kmol) | t_{bi} | t_{mi} | h_i (kJ/mol) | g_f (kJ/mol) | h_{ci} (kJ/mol) | n |
|--------|---------------------|----------------------|--------|--------|-------------|-------------|----------------|---|
| 1.6781 | 0.019904            | 0.07504              | 0.8894 | 0.464  | -45.947     | -8.03       | 4.116          | 2  |
| 3.492  | 0.010558            | 0.05576              | 0.9225 | 0.9246 | -20.763     | 8.231       | 4.65           | 2  |
| 4.033  | 0.001315            | 0.03153              | 0.6033 | 0.3557 | -3.766      | 19.848      | 2.771          | 3  |
| 4.8823 | -0.010404           | -0.00034             | 0.2878 | 1.6479 | 17.119      | 93.745      | 1.284          | 1  |
| 8.9582 | 0.01259             | 0.07327              | 1.7957 | 2.0018 | 64.145      | 88.402      | 6.797          | 1  |
| 9.7292 | 0.005148            | 0.03897              | 3.2152 | 3.5979 | -181.422    | -158.589    | 24.529         | 1  |

### First-order groups

| 4-ring | 6-ring | CH-CH_{m}=CH_{a} | CH_{m,cyclic}-OH |
|--------|--------|------------------|------------------|
| -1.2978 | 0.847999 | -0.385          | 0.3233          |
| 0.001171 | 0.002257 | 0.005675       | 0.006917       |
| -0.00851 | 0.01636  | 0.00826        | -0.02297       |
| 0.3563   | 0.1957   | -0.09          | -0.069         |
| 99.455   | 1.5656   | -0.2361       | 9.5209         |
| 92.573   | -9.66    | 4.504         | -16.333        |
| 1        | 1        | 2              | 1               |

### Second-order groups

| Properties | \( T_c (K) \) | \( P_c \) (bar) | \( V_c \) (m^{3}/kmol) | \( T_b (K) \) | \( T_m (K) \) | \( \Delta H_{f,298} \) (kJ/mol) | \( \Delta G_{f,298} \) (kJ/mol) | \( \Delta H_{v,298} \) (kJ/mol) |
|------------|---------------|-----------------|------------------------|---------------|---------------|---------------------------------|---------------------------------|---------------------------------|
|            | 689.9        | 27.91           | 0.4651                 | 490.7         | 315.2         | -151.57                         | 149.61                          | 69.70                           |

### 1.4. Ghasemitabar- Movagharnejad method (GM)

The Ghasemitabar-Movagharnejad method (GM) is an improved second order group contribution method developed to determine the normal boiling point \( T_b \) of organic compounds by Eq. (S20) to Eq. (S24). This method is based on the Joback's first order functional groups with some changes and some newly added functional groups developed from experimental data. Contribution values are optimized using 2036 experimental data of organic components ranging from 1-36 carbon atoms and molecular weight 26-555 (g mol\(^{-1}\)), including heavy and complex polycyclic aromatic compounds. In this method, it is tried to distinguish most of the structural isomers and stereoisomers by second order functional groups. First and second order functional groups of the hydrocarbons and hydrocarbon derivatives containing carbon, hydrogen, oxygen, nitrogen, sulfur, fluorine, chlorine, bromine and iodine atoms, are also included. The results of the new method are compared to several well-known methods. The average absolute relative deviation of normal boiling point predictions for 2036 organic compounds is 1.01075\% [4].

\[
T_b(K) = T_1(K) + T_2(K) \tag{S20}
\]
\[ T_1(K) = \sum_i N_i(t_{bi}) + Q_1 \sum_j N_j(t_{bj}) \] (S21)

\[ T_2(K) = Q_2(aM_W^3 + bM_W^2 + cM_W) + d \] (S22)

\[ Q_1 = N_C + \sum_{i=1}^{N_A} X_i U_i \] (S23)

\[ Q_2 = N_C + \sum_{i=1}^{N_A} X_i V_i \] (S24)

1.5. Tahami-Movagharnejad-Ghasemitabar (TMG)

The Tahami-Movagharnejad-Ghasemitabar method (TMG) is an improved second order group contribution method developed to estimate critical constants (temperature, pressure, and volume) of organic compounds by Eq. (S25) to Eq. (S38). The functional groups of Joback and Reid method are employed with some changes as first order functional groups and some second order functional groups are also defined and added to them. The critical constants of most structural isomers and stereoisomers are distinguished in this method by considering the second order functional groups. The hydrocarbons and hydrocarbon derivatives considered in this research include carbon, hydrogen, oxygen, nitrogen, sulfur, fluorine, chlorine, bromine, and iodine atoms. The percentage of the average absolute relative deviations are 1.12\% for critical temperature, 2.69\% for critical pressure, and 2.67\% for critical volume [5].

For critical temperature:

\[ T_C = C \left[ \ln \left( S_{T1} + S_{T1} \left( \sum_i N_i T_{ci} \right) + \left( \sum_i N_i T_{ci} \right)^2 \right) + \left( \sum_j N_j T_{cj} \right)^2 \right] \] (S25)

\[ C = a + b T_b + c T_b^2 + d T_b^3 \] (S26)

\[ S_{T1} = \sum_{k=1}^{N_A} s_{T1k} + \ln (N_{atoms}) \] (S27)

\[ S_{T2} = \sum_{k=1}^{N_A} s_{T2k} + \ln (N_{atoms}) \] (S28)
For critical pressure:

\[
P_C = C \left[ \left( S_{P1} + S_{P2} \left( \sum_{i} N_i P_{ci} \right) + \left( \sum_{i} N_i P_{ci} \right)^2 \right)^{-1} + \left( S_{P3} + S_{P4} \left( \sum_{j} N_j P_{cj} \right) + \left( \sum_{j} N_j P_{cj} \right)^2 \right)^{-1} \right]^{-1} \tag{S29}
\]

\[
C = \frac{\exp \left( a_1 + b_1 T_b \right)}{a_2 + b_2 M_W} \tag{S30}
\]

\[
S_{P1} = \sum_{k=1}^{N_A} s_{P1k} \tag{S31}
\]

\[
S_{P2} = \sum_{k=1}^{N_A} s_{P2k} \tag{S32}
\]

\[
S_{P3} = \sum_{k=1}^{N_A} s_{P3k} \tag{S33}
\]

\[
S_{P4} = \sum_{k=1}^{N_A} s_{P4k} \tag{S34}
\]

\[
S_{P5} = \sum_{k=1}^{N_A} s_{P5k} \tag{S35}
\]

For critical volume:
\[ V_C = \sum_i N_i V_{ci} + \left( S_{V1} + \sum_j N_j V_{cj} \right) N_{atoms} + S_{V2} N^2_{atoms} \]  
(S36)

\[ S_{V1} = \sum_{k=1}^{N_A} S_{V1k} \]  
(S37)

\[ S_{V2} = \sum_{k=1}^{N_A} S_{V2k} \]  
(S38)

1.6. Abdi-Movagharnejad-Ghasemitabar method (AMG)

The Abdi-Movagharnejad-Ghasemitabar method (AMG) is a new group contribution method developed by Abdi et al. to estimate enthalpy of vaporization at normal boiling temperature \( \Delta H^o_{vb} \) (kJ mol\(^{-1}\)) of organic compounds by Eq. (S39) to Eq. (S40). The new group contribution method is a modification to the Joback-Reid method and gives more accurate estimations of the enthalpy of vaporization at normal boiling temperature of organic compounds. Group contribution values are optimized using 3950 experimental data of organic components with a molecular weight range of 28-565 (g mol\(^{-1}\)) and number of carbon atoms range of 1-40. The results of the new method on 3950 different organic compounds shows a percentage average relative error of 1.683%.

\[ \Delta H^o_{vb} = C + \sum_i n_i (\Delta H_{vb})_i + \sum_j n_j (\Delta H_{vb})_j \]  
(S39)

\[
C = a + b M_W + c M_W^2 + d M_W^3
\]  
(S40)

In equation (S39), \( n_i \) indicates the number of times the first-level group \( i \) appears in the molecular structure, \((\Delta H_{vb})_i\) is the first order group contribution of type \( i \), \( n_j \) indicates the number of times the second-level group \( j \) appears in the molecular structure, \((\Delta H_{vb})_j\) is the second-order group contribution of type \( j \) and \( M_W \) is the molecular weight of the desired compound. The parameters \( a, b, c, d \) in equation (S40) are optimized for each molecular weight range and are presented in the literature [6].

The first-level and second-level order group contributions data and the values of the additional adjustable parameters for the methods TMG and AGM are presented in their main references.
the selected set of terpenes the constant parameters are listed in Table S2. Table S3 shows an application example of the previous methods in the estimation of α-pinene epoxide properties. Table S5 to Table S7 summarize the results of the application of the previous methods in the properties estimation of the selected terpenes, including the Ruzicka method (see main reference for development).

**Table S2.** Values of the additional adjustable parameters for the methods TMG and AGM for the set of selected terpenes.

| Parameter | \( T_b \) | \( T_c \) | \( \Delta H_{v298} \) |
|-----------|----------|----------|------------------|
| \( T_b \) | 80 ≤ \( M_w \) < 140 | 140 ≤ \( M_w \) < 190 | 350 ≤ \( T_b \) ≤ 500 | \( 500 \leq T_b \leq 680 \) | \( 400 \leq T_b \leq 530 \) | \( 100 \leq M_w \leq 150 \) | \( 150 \leq M_w \leq 200 \) | \( 100 \leq M_w \leq 230 \) |
| \( a \) | -2.47E-06 | -1.00E-06 | 23.50322 | 24.00654 | 2.15E-10 | - | - | 16.224 |
| \( b \) | 2.78E-04 | -3.18E-05 | 0.24955 | 0.25571 | 8.51E-04 | - | - | 0.073 |
| \( c \) | 3.49E-02 | 5.58E-02 | -2.83E-05 | -3.98E-05 | - | 0.34583 | 0.321 | -1.76E-04 |
| \( d \) | 199.26548 | 189.14878 | 4.69E-08 | 3.53E-08 | - | 1.06E-04 | 2.53E-04 | -4.34E-08 |

**Method**

| \( s_{1k} \) | \( s_{2k} \) | \( s_{3k} \) | \( s_{4k} \) | \( s_{5k} \) | \( s_{6k} \) | \( s_{7k} \) | \( s_{8k} \) | \( U_{i-C} \) | \( U_{i-O} \) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| C | 124.65149 | -19.3004 | 0.03701 | 0.38302 | 1.05351 | 1.58913 | -0.0843 | -0.03196 | 0.0687 |
| H | 9.78975 | 2.84E-07 | -0.0055 | 0.00497 | -0.02629 | 0.06404 | -0.23924 | -0.0801 | 2.77E-04 | V_{i-C} | 0.84921 |
| O | -4.31095 | 1.03728 | 2.58E-12 | 0.2359 | 0.21805 | 0.00548 | 0.00503 | -0.117E-05 | -3.40E-08 | V_{i-O} | -1.36996 |

*For critical pressure estimation \( a = a_1, b = b_1, c = a_2 \) and \( d = b_2 \).

**Table S3.** Example of α-Pinene epoxide properties estimation by Ghasemitabar-Movagharnejad et al. methods.

| \( T_{ci} (K) \) | \( P_{ci} \) (bar \( 0.5 \)) | \( V_{ci} \) (cm\(^3\)/mol) | \( T_{bi} (K) \) | \( \Delta H_{ubi} \) | \( n \) |
|----------------|----------------|----------------|----------------|----------------|------|
| α-Pinene epoxide | | | | | |
| \( CH_3 \) (1) | 0.11478 | 0.04023 | 72.56818 | 13.0945 | 0.965 | 3 |
| \( CH_2 \) (ss) (2) | -0.10066 | 0.0212 | 43.1586 | 23.3777 | 1.74 | 2 |
| \( CH \) (ss) (3) | 0.14457 | 0.01776 | 33.80241 | 20.1251 | 1.591 | 3 |
| \( C \) (ss) (4) | 0.25246 | 0.00246 | 25.56758 | 17.7436 | 0.924 | 2 |
| Substance                        | \(C_v,298.15\)/\(R\) | \(C_v,298.15\)/(J mol\(^{-1}\) K\(^{-1}\)) | \(C_p,298.15\)/\(R\) | \(C_p,298.15\)/(J mol\(^{-1}\) K\(^{-1}\)) | \(S^o,298.15\)/(J mol\(^{-1}\) K\(^{-1}\)) |
|---------------------------------|-----------------|---------------------------------|-----------------|---------------------------------|------------------|
| \(\alpha\)-Pinene epoxide      | 19.79           | 164.56                          | 20.79           | 172.88                          | 380.62            |
| Campholenic aldehyde           | 21.42           | 178.11                          | 22.42           | 186.44                          | 429.70            |
| Fencholenic aldehyde           | 21.51           | 178.78                          | 22.51           | 187.11                          | 441.29            |
| trans-\(\alpha\)-Carveol       | 19.27           | 160.21                          | 20.27           | 168.53                          | 398.48            |
| Pinocarveol                    | 20.72           | 172.21                          | 21.72           | 180.54                          | 397.44            |
| Isopinocamphone                | 21.16           | 175.90                          | 22.16           | 184.22                          | 422.63            |
| \(\beta\)-Pinene epoxide      | 20.43           | 169.87                          | 21.43           | 178.20                          | 396.60            |
| Myrtenol                       | 19.65           | 163.34                          | 20.65           | 171.63                          | 392.25            |
| Perillyl alcohol               | 19.40           | 161.29                          | 20.40           | 169.58                          | 385.43            |
|                                | 20.92           | 173.89                          | 21.92           | 182.21                          | 427.73            |

\(a\)The values of \(C_p,298.15\) were calculated with the relation: \(C_p - C_v = R\).
Table S5. Critical properties and acentric factor of terpenes present in α- and β-pinene epoxides isomerization.

| Substance/Method       | Property     | $T_{c,i}$ / K | $p_{c,i}$ / bar | $v_{c,i}$ / (m$^3$ kmol$^{-1}$) | $Z_{c,i}$ | $\omega_i$ | Ref.  |
|------------------------|--------------|---------------|----------------|---------------------------------|----------|-----------|--------|
|                         |              | JR      | CG   | TMG   | J*   | Avg.   | Ref.      | JR     | CG   | TMG   | J*   | Avg.   | Def*   | Ref.      | Def*   |
| α-Pinene               |              | 655.1   | 631.0| 715.9| 644.0| 661.5±38| 632       | 28.9   | 26.8 | 34.3 | 27.6 | 29.4±3.4 | 27.6   |
| β-Pinene               |              | 648.5   | 640.7| 675.9| 643.0| 652.0±16| 643       | 28.8   | 29.3 | 31.6 | 27.6 | 29.3±1.7 | 27.6   |
| α-Pinene epoxide       |              | 676.8   | 649.9| 663.2| 676.5| 666.6±13| -         | 30.9   | 31.8 | 27.3 | 30.9 | 30.2±2   | -      |
| β-Pinene epoxide       |              | 694.6   | 661.0| 729.2| 694.3| 694.8±28| -         | 33.0   | 30.2 | 31.8 | 33.0 | 32.0±1.4 | -      |
| trans-Carveol          |              | 731.9   | 695.0| 734.3| 731.7| 723.2±19| -         | 29.3   | 27.6 | 29.6 | 29.3 | 29.0±0.9 | -      |
| Isopinocamphone        |              | 727.9   | 624.9| 794.2| 727.6| 718.6±70| -         | 28.3   | 31.6 | 29.2 | 28.3 | 29.4±1.6 | -      |
| Pinocarveol            |              | 723.3   | 689.9| 689.2| 723.1| 706.4±19| -         | 30.8   | 27.9 | 29.9 | 30.8 | 29.8±1.3 | -      |
| Fencholic aldehyde     |              | 698.0   | 661.3| 677.2| 697.7| 681.1±20| -         | 28.0   | 24.5 | 29.1 | 28.0 | 27.4±2   | -      |
| Campholic aldehyde     |              | 698.0   | 661.3| 672.3| 697.7| 682.4±18| -         | 28.0   | 24.5 | 29.3 | 28.0 | 27.4±2.1 | -      |
| Perillyl alcohol       |              | 736.8   | 702.5| 746.7| 736.5| 730.6±19| -         | 30.4   | 24.1 | 28.2 | 30.4 | 28.3±3   | -      |
| Myrtanal               |              | 696.5   | 663.5| 747.9| 696.2| 701.0±35| -         | 29.5   | 30.1 | 32.2 | 29.5 | 30.4±1.3 | -      |
| Myrtenol               |              | 734.4   | 685.3| 825.6| 734.2| 744.9±59| -         | 32.0   | 28.4 | 31.9 | 32.0 | 31.1±1.8 | -      |

[511]
| Myrtenol | 0.504 | 0.501 | 0.401 | 0.504 | 0.477±0.051 | - | 0.264 | - | 0.775 | - |

JR: Joback-Reid, CG: Constantinou-Gani, TMG: Tahami-Movagharnejad-Ghasemitabar, J*: Joback from Aspen Plus, Avg.: average, Ref.: references simulated or obtained experimentally [7]. Def*: estimated by definition equations from critical properties in Aspen Plus.
Table S6. Phase change properties of terpenes present in α- and β-pinene epoxides isomerization.

| Property            | \( T_{b,i} / K \) | \( \Delta H_{fus,i} / (kJ \text{ mol}^{-1}) \) |
|---------------------|-------------------|-----------------------------------------------|
|                     | JR    | CG   | GM   | J*   | Avg. | Ref. | JR    | CG   | AMG  | R*   | Avg. | Ref. |
| \( \alpha \)-Pinene | 445.9 | 429.8| 409.1| 429.3| 428.5±15 | 428.0 [8] | 429 [9] | 430 [10] | 436 [11] | 37.35 | 42.5 | 36.41 | 38.36±3 | 44.6±0.1 [12] | 45.4 [13] |
| \( \beta \)-Pinene  | 440.9 | 428.9| 418.0| 439.2| 431.8±11 | 439.15 [14] | 36.55 | 41.7 | 37.92 | 36.82 | 38.25±2 | 45.8±0.1 [12] |
| \( \alpha \)-Pinene epoxide | 462.4 | 459.0| 447.0| 462.2| 455.6±8 | - | 39.01 | 44.2 | 40.66 | 41.17±2 | 42.0±4 |
| \( \beta \)-Pinene epoxide | 471.4 | 468.5| 457.7| 471.2| 467.2±6 | - | 39.49 | 48.3 | 39.80 | 41.97 | - |
| \( \text{trans} \)-Carveol | 536.2 | 485.1| 515.3| 536.0| 518.1±24 | 499.7 [16] | 55.02 | 69.1 | 48.13 | 44.00 | 57.01±9 | - |
| Isopinocamphone | 504.9 | 417.7| 482.0| 504.7| 477.3±41 | - | 40.33 | 37.9 | 43.64 | 44.73 | 41.65±3 |
| Pinocarveol | 528.4 | 490.7| 472.7| 528.2| 505.0±28 | - | 52.92 | 69.7 | 44.00 | 55.54 | 55.54±11 | - |
| Fencholenic aldehyde | 492.1 | 472.2| 450.0| 491.9| 476.5±20 | - | 44.33 | 53.0 | 41.43 | 45.26 | 45.9±5 | - |
| Camoholenic aldehyde | 492.1 | 472.2| 450.3| 491.9| 476.6±20 | - | 44.33 | 53.0 | 40.56 | 45.26 | 45.77±5 | - |
| Perillyl alcohol | 540.8 | 504.2| 520.0| 540.6| 526.4±18 | - | 55.33 | 70.0 | 47.50 | 57.41 | 57.55±9 | - |
| Myrtanal | 485.7 | 469.3| 476.3| 485.5| 479.2±8 | - | 42.80 | 50.8 | 43.13 | 44.37 | 45.28±4 | - |
| Myrtenol | 538.0 | 495.9| 493.0| 537.8| 516.2±25 | 494.7 [16] | 54.03 | 66.9 | 44.11 | 57.83 | 55.72±9 | - |

| Property            | \( T_{fus,i} / K \) | \( \Delta H_{fus,i} / (kJ \text{ mol}^{-1}) \) |
|---------------------|-------------------|-----------------------------------------------|
|                     | JR    | CG   | Aspen | Avg. | Ref. | JR | Aspen | Avg. |
| \( \alpha \)-Pinene | 267.8 | 220.3| 209.15| 232.4±25 | 197.64 [17] | 11.43 | 12.10 | 11.77±3 |
| \( \beta \)-Pinene  | 268.2 | 222.8| 211.61| 234.2±24 | 210.35 [18] | 9.44 | 10.30 | 9.87±0.4 |
| \( \alpha \)-Pinene epoxide | 325.7 | 274.5| - | 300.1±26 | - | 15.69 | - | 15.69 |
| \( \beta \)-Pinene epoxide | 326.4 | 267.7| - | 297.0±29 | - | 12.52 | - | 12.52 |
| \( \text{trans} \)-Carveol | 264.0 | 297.8| - | 280.9±17 | - | 16.89 | - | 16.89 |
| Isopinocamphone | 318.5 | 216.0| - | 267±25 | - | 11.18 | - | 11.18 |
| Pinocarveol | 324.7 | 315.2| - | 320.0±5 | - | 14.60 | - | 14.60 |
| Fencholenic aldehyde | 288.3 | 251.5| - | 269.9±18 | - | 13.49 | - | 13.49 |
| Camoholenic aldehyde | 288.3 | 251.5| - | 269.9±18 | - | 13.49 | - | 13.49 |
| Perillyl alcohol | 268.2 | 226.3| - | 247.2±21 | - | 15.82 | - | 15.82 |
|     | Myrtanal |     | Myrtenol |     |
|-----|----------|-----|----------|-----|
| JR  | Joback-Reid | CG  | Constantinou-Gani | GM   | Ghasemitabar-Movagharnejad |
| J*  | Joback from Aspen Plus | AMG | Abdi-Movagharnejad-Ghasemitabar | R*  | Ruzicka method from Aspen Plus |
| Avg. | average | Ref. | references simulated or obtained experimentally |
|     | 292.2 | 272.7 | - | 282.5±10 | - | 13.96 | - | 13.96 |
|     | 328.6 | 255.0 | - | 291.8±37 | - | 15.52 | - | 15.52 |
Table S7. Constants of liquid heat capacities simulation of the terpenes present in α- and β-pinene epoxides isomerization. Aspen Plus, Ruzicka method [19].

\[
C_{pl,i} / (J \text{ kmol}^{-1} \text{ K}^{-1}) = a_i + b_i T + c_i T^2
\]

| Substance            | \(a_i\)   | \(b_i\)   | \(c_i\)   | ΔT / K  |
|----------------------|-----------|-----------|-----------|---------|
| α-Pinene             | 151113.309| -289.73074| 1.85386301| 237.4 - 429.3 |
| β-Pinene             | 136582.04 | -151.532776| 1.61221425| 242.9 - 439.2 |
| α-Pinene epoxide     | 183798.563| -488.501575| 2.30909574| 255.6 - 462.2 |
| β-Pinene epoxide     | 179006.91 | -375.722729| 2.0235921 | 260.6 - 471.2 |
| trans- Carveol \(a\) | -63528.27 | 789.0699  | 0.15321   | 264 – 534.5 |
| Isopinocamphone      | 220996.849| -134.749938| 1.16123606| 279.1 - 504.7 |
| Pinocarveol \(a\)    | -105351.25| 991.2487  | -0.02117  | 319.2 - 529 |
| Fencholenic aldehyde | 144928.228| 335.093876| 0.528114395| 272.0 - 491.9 |
| Campholenic aldehyde | 144928.228| 335.093876| 0.528114395| 272.0 - 491.9 |
| Perillyl alcohol     | -11623.5187| 1280.65238| -0.68735971| 299.0 - 540.6 |
| Myrtenal             | 96514.4995 | 364.368435| 0.627502721| 268.5 - 485.5 |
| Myrtenol             | -65231.9039| 1257.0982 | -0.248119945| 297.4 - 537.8 |

\(a\) Obtained by regression of the liquid heat capacity data within the software Aspen Plus.
Figure S1. Tendencies of enthalpy and Gibbs free energy of reaction as a function of dielectric constant for a) α-pinene epoxide isomers and b) β-pinene epoxide isomers.

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