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Study of solvents effect on distribution of configurational and conformational isomers of apo-tirucallol theoretically and experimentally

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ABSTRACT

(2*S*,3*R*)-2-(2-Hydroxypropan-2-yl)-5-methyltetrahydro-2*H*-pyran-2,3-diol and its configurational isomer (2*R*,3*R*)-2-(2-hydroxypropan-2-yl)-5-methyltetrahydro-2*H*-pyran-2,3-diol were used in the distribution analyses of configurational and conformational isomers for the identification of 1α,7α-diacetoxyl-17α-20*S*-21,24-epoxy-apo-tirucall-14-ene-3α,23*R*,24*S*,25-tetraol in methanol, chloroform and acetone solvents, respectively. The geometries of configurational and the corresponding conformational isomers were optimized through B3LYP/6-31G(d) and MP2/6-311+G(d) tests in the gas phase and in the three solvents, respectively. PCM and CPCM models were used, respectively. Distributions of different isomers in the three solvents were finally examined by ^{1}H NMR spectra. Two computational methods were found to give the good predictions of distribution of the configurational and conformational isomers in the three solvents.

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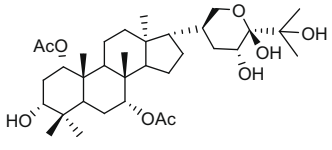
1. Introduction

Distribution of different conformations in a solution normally decides a reaction's potential [1–3], such that the enantioselectivity is greatly affected by the distribution of free chiral ligand conformations in the enantioselective additions of diethylzinc on benzaldehyde [1]. The dynamic investigations of conformations have achieved great progress by using NMR or HPLC method [3–21]. During the last decades, Lunazzi, Mazzanti, Casarini and coworkers have reported a series of conformational studies with some interesting discoveries [5–9]. Agranat has reported the dynamic stereochemistry of overcrowded homomerous bistricyclic aromatic enes [10]. The isomerizations of 4-methylphenoxyimidoyl azides have also been reported using dynamic ^{1}H NMR [11]. Static conformational analyses of acylated tetrahydrobenzazepines have been performed [12]. Conformational studies of other compounds, such as the bioactive cyclic heptapeptide from marine origin [13], acyclic hydrazines [14], etc. have been done [15–20]. Among the compounds, the condensation products from ketone/aldehyde with alcohols are well known in organic chemistry. This condensation can result in different configurational isomers. The equilibrium between the different configurational isomers changes with the solvent change. Each configurational isomer has some stable conformational isomers in solutions. It is rare to find a natural product having such an unstable equilibrium which changes with different configurational and conformational isomers in different solvents.

In our previous study [21], the absolute configuration of compound **1** had been examined by X-ray crystallography. The solvent for its re-crystallization was water unexpectedly instead of organic solvents. This could hint at compound **1** that could have either major fractions, or low solubility in water or both. Theoretically, **1** could form two configurational isomers due to the ring-open and ring-close reactions with the semi-lactone, and each of the two isomers could form conformational isomers in solution. To investigate the distributions of configurations and conformations of **1** in different solvents, the model molecule **2** was selected for the distribution study. The computational results exhibited that the distribution of configurational isomers had undergone big changes in different polar solvents, such as methanol, chloroform and acetone. To confirm which predictions were correct, normal ^{1}H NMR tests, rather than the dynamic NMR techniques, were used to determine the distributions between two configurational isomers in the three solvents. The experimental results confirmed the suitable method was B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) or MP2/6-311++G(d,p)//B3LYP/6-31G(d) using PCM or CPCM models, respectively, instead of the MP2/B3LYP/6-311++G(d,p)//MP2/6-311+G(d) method using molecule **2** as the model.



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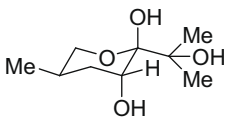

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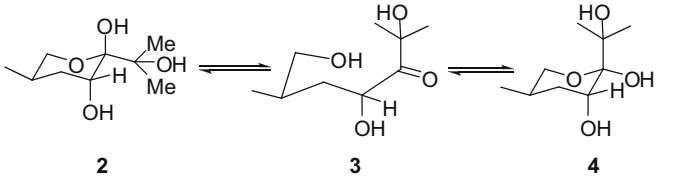
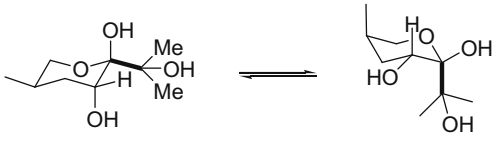
2. Computational method

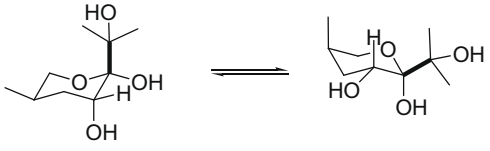
Model **2** was selected for the computations based on the structure **1**. Isomerization of **2** could yield another configurational isomer **4** via the ring-open reaction to **3** (Eq. (1)). Isomer **2** could form another relatively stable conformation **5**, and **4** could form **6** in solutions (Eqs. (2) and (3)), respectively. The equilibriums between **2** and **5**, **4** and **6** depended on their relative energies released in the solution.



2 **3** **4** (1)



2 **5** (2)



4 **6** (3)

Due to the rotation of free single bond (the bold bond in **2**, **4**–**6**), there would be three relative stable conformations, **a**, **b** and **c**, for two conformations, **2** and **5**, see the following Newman structures, and **d**, **e** and **f** for **4** and **6**, respectively (Fig. 1).

The ratio of the two configurational isomers observed in ^{1}H NMR would be the sum of quantity of conformations **2** and **5** divided by the sum of quantity of conformations **4** and **6**. All possible conformations were investigated since there was a big –CMe_2OH group connected to the semi-lactone ring, whose effects on the relative energy were unknown. The relative energies for all conformations were computed in the gas phase first by the B3LYP/6-31G(d) method using Gaussian 03 package [22]. These results have been summarized in Table 1. The energy magnitudes of **4e**, **5a**, **5b** and **5c** are 14.227, 10.227, 12.336 and 18.223 kcal/mol (Table 1, entries 2 and 3), respectively. The large energy difference values exhibiting these conformations would have very little distribution in solutions. Therefore, these four conformations were not used in further calculations.

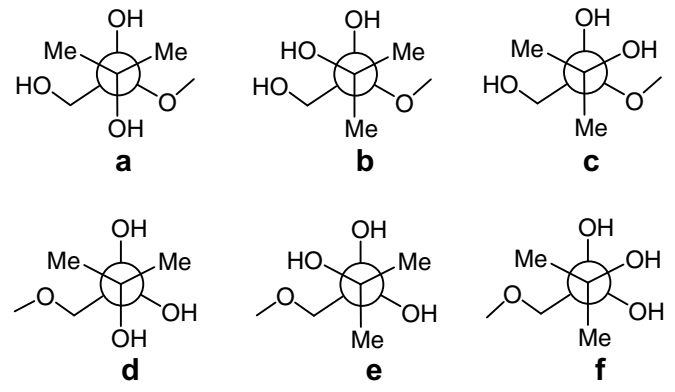


Fig. 1. The Newman structures, **a**–**c** in conformations **2** and **5** and **d**–**f** in **4** and **6**.

Table 1
The relative energy magnitudes of all conformations obtained through at the B3LYP/6-31G(d) method in the gas phase (with energies in kcal/mol)

Entry	Conformation	Relative energy					
		a	**b**	**c**	**d**	**e**	**f**
1	**2**	5.186	4.637	1.992	–	–	–
2	**4**	–	–	–	4.839	14.227	4.158
3	**5**	10.227	12.336	18.223	–	–	–
4	**6**	–	–	–	1.206	3.547	0.000[a]

[a] The energy of −654.67695 (au) was used as the reference zero-point in the relative energy computations.

The geometries of all eight conformations which had less than 10 kcal/mol energy difference, **2a**–**2c**, **4d**, **4f** and **6d**–**6f**, were further optimized at the MP2/6-311+G(d) level in the gas phase. Frequency computations were performed for each conformation. Free energetics in the gas phase and in solutions, energetics after zero-point energy corrections were used in the relative energy calculations for all eight conformations. The B3LYP/6-31++G(d,p) and MP2/6-31++G(d,p) methods were selected for the single point energy (SPE) correction computations in methanol, chloroform and acetone solvents, respectively, using PCM and CPCM models. Furthermore, full optimization of the eight conformations was performed by the B3LYP/6-31G(d) method in the three solvents, respectively, using PCM model. The ^{1}H NMR tests were carried out to test which method provided the suitable predictions of distributions of the configurational and conformational isomers. Finally, the best method was selected for distribution computations of the configurational isomers in water.

3. Results and discussions

The relative energies in three solvents using B3LPY and MP2 theory at the 6-31++G(d,p) basis of sets using B3LYP/6-31G(d)-optimized geometries have been summarized in Table 2. The PCM model was used in the calculations. The lowest energy conformation in different solvents in the liquid phase was different from that in the gas phase. For example, the lowest energy conformation in the gas phase was **6f** (Table 1, entry 4). However, the lowest energy conformation in methanol was **2c** in three solvents (Table 2, entry 3). It would have caused blunders if the lowest energy conformation had been used as the geometries in the ratio computations in different solvents in the gas phase. The distributions of these conformations in three solvents were computed using Boltzmann formula. The results have been summarized in Table 2. The ratio of total distribution of conformation **2** to that of conforma-

Table 2
The relative SPE magnitudes in three solvents using B3LPY and MP2 theory at the 6-31++G(d,p) basis of sets using B3LYP/6-31G(d)-optimized geometries (with energy in kcal/mol)

Entry	Conf. no.	ΔE in MeOH		ΔE in $CHCl_3$		ΔE in MeCOMe	
		B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
1	**2a**	2.348	3.012	2.698	3.338	2.127	2.791
2	**2b**	3.009	3.428	3.022	3.452	2.700	3.117
3	**2c**	0.000	0.000	0.000	0.000	0.000	0.000
4	**4d**	2.554	3.362	2.723	3.533	2.474	3.289
5	**4f**	3.657	4.458	2.936	3.720	3.223	4.022
6	**6d**	2.415	2.156	1.878	1.604	2.474	2.219
7	**6e**	2.623	2.716	2.606	2.693	2.527	0.618
8	**6f**	1.205	1.085	0.313	0.153	1.106	0.984
9	Ratio of **2:(4 + 6)**	**5.2:1.0**	**5.0:1.0**	**1.5:1.0**	**1.2:1.0**	**5.1:1.0**	**4.4:1**

tions **4** and **6** in three solvents have been listed at the bottom of Table 2 (entry 9). The ratios of the two configurational isomers (**2** versus **4** and **6**) were 1.5:1, 5.1:1 and 5.2:1 using B3LYP/6-311++G(d,p) method with solvents changed from chloroform to acetone to methanol, respectively (Table 2, entry 9). The ratios were 1.2:1, 4.4:1 and 5.0:1, respectively, using MP2/6-311++G (d,p) method in the above case. It shows that the higher the polarity of solvent is, the higher the fraction of **2** is in a solvent.

As mentioned above, the lowest energy conformation in the gas phase was different from that obtained in the liquid phase. Thus, if not every low energy conformation was investigated, the distribution prediction could have a big difference from that obtained using all conformations. For example, if only **2b** and **6f** were considered in the distribution computations, the ratios would be 7.7:1, 1.7:1 and 6.5:1 in methanol, chloroform and acetone, respectively, by the B3LYP/6-311++G(d,p) method. The ratios became 6.3:1, 1.3:1 and 5.3:1, respectively, using MP2/6-311++G(d,p) method. The ratios in chloroform (1.7:1 at the B3LYP/6-311++G(d,p) level, or 1.3:1 at the MP2/6-311++G(d,p) level) were close to those obtained using all conformations. However, the ratios in methanol and acetone maintained a significant difference. For example, the ratios changed from 5.2:1 to 7.7:1 in methanol, or from 5.1 to 6.5 in acetone if two conformations had been used in the B3LYP/6-311++G(d,p) method. The greater the polarity of a solvent is, the bigger the errors are found in distribution computations.

The ratios in solutions were calculated once again using the total free energy magnitudes and the PCM model, and have been summarized in Tables 3 and 4. The fraction of configurational isomer **2** (entry 9 in Table 3) was double to that obtained in using the SPE in the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) method using PCM model (entry 9 in Table 2). The fraction of **2** was seven times bigger (entry 9 in Table 4) than that obtained by the MP2/6-311++G(d,p)//B3LYP/6-31G(d) method (entry 9 in Table 2).

Table 3
Relative free energy magnitudes in solutions by the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) method using PCM model, and the ratios between two configurational isomers (with energies in kcal/mol)

Entry	Conf. no.	In methanol	In acetone	In chloroform
1	**2a**	2.517	2.290	2.858
2	**2b**	2.942	2.636	2.955
3	**2c**	0.000	0.000	0.000
4	**4d**	2.514	2.440	2.681
5	**4f**	3.722	3.292	2.989
6	**6d**	2.706	2.745	2.112
7	**6e**	2.997	2.876	2.923
8	**6f**	1.621	1.493	0.657
9	Ratio of **2**:(**4** + **6**)	10.5:1	8.8:1	2.7:1

Table 4
Relative energy magnitudes in solutions by the MP2/6-311++G(d,p)//B3LYP/6-31G(d) method using PCM model, and the ratios between two configurational isomers (with energy in kcal/mol)

Entry	Conf. no.	In methanol	In acetone	In chloroform
1	**2a**	1.898	1.662	2.331
2	**2b**	2.461	2.127	2.478
3	**2c**	0.000	0.000	0.000
4	**4d**	2.801	2.706	2.994
5	**4f**	4.821	4.356	4.034
6	**6d**	3.677	3.712	3.095
7	**6e**	2.925	2.804	2.869
8	**6f**	2.543	2.404	1.528
9	Ratio of **2**:(**4** + **6**)	33.2:1	28.0:1	10.8:1

The MP2/6-311+G(d) theory was used in optimizations in the gas phase for all eight conformations. The computed geometries were then used for the SPE computations in different solvents using a PCM model. The relative energetics of these conformations in the three solvents was computed via Boltzmann formula, and these results have been summarized in Table 5. The ratios of configurational isomers which were computed using those relative energies have also been listed in Table 5.

The ratios of **2** to (**4** + **6**) were 5.4:1 and 2.8:1 in methanol obtained through B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) methods, respectively, using the MP2/6-311+G(d)-optimized geometries. However, the sequence in chloroform and acetone reversed from 1.2:1 and 4.4:1, to 1:1.7 and 1:1.3 using MP2/6-311++G(d,p)//B3LYP/6-31G(d) and MP2/6-311++G(d,p)//MP2/6-311+G(d) methods, respectively (Table 5, entry 9). The total free energy data in solutions were also used in the ratio computations in order to compare the differences with that obtained using SPE in the Boltzmann computations. These results have been listed in Tables 6 and 7. Again, the faction of **2** obtained using the SPE data were bigger than those obtained using total free energy in solutions (at the bottom of Tables 6 and 7). The distributions of the configurational isomer **2** in the polar solvent occupied more fractions than in the non-polar solvent.

To further investigate the configurational ratio in different solvents, the energy computations were carried out by B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) methods, respectively, using the B3LYP/6-31G(d)- and MP2/6-311+G(d)-optimized geometries via CPCM model. These computational results have been listed in the Tables 8 and 9, respectively. The SPE magnitudes were used in the energy calculations. The fraction of the configurationally isomer **2** obtained via CPCM increased to 10% in all cases.

The sequences of the ratios in the three solvents using CPCM and B3LYP/6-31G(d)-optimized geometries were the same as those obtained using PCM model. However, the disagreement between the ratios obtained through the MP2/6-311++G(d,p) method reappeared using the MP2/6-311+G(d)-optimized geometries.

The total free energetics in a solution were also used in the ratio computations, and the results have been summarized in Table 10. Again, the fraction of configurational isomer **2** occupied more percentage than the sum of isomers of **4** and **6** when total free energy data in solutions were used in the MP2/6-311++G(d,p) methods. Especially, when the B3LYP/6-31G(d)-optimized geometries were used, the fraction of **2** occupied much space than the sum of isomers of **4** and **6** (Table 10, entry 4).

To further investigate the effect of solvents on the distributions, the conformations were optimized in methanol, chloroform and acetone solvent in the B3LYP/6-31G(d) method, using PCM model, respectively. The SPE and total free energy data in a solution were used in distribution calculations. The ratios of the configurational

Table 5
Relative energy values in three solvents using B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) methods and PCM model (with energy in kcal/mol). MP2/6-311+G(d)-optimized geometries were used

Entry	Conf. no.	ΔE in MeOH		ΔE in MeCOMe		ΔE in $CHCl_3$	
		B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
1	**2a**	0.339	0.570	0.000	0.442	0.210	0.697
2	**2b**	3.133	3.564	2.754	3.400	2.940	3.657
3	**2c**	0.000	0.000	0.134	0.364	0.370	0.663
4	**4d**	2.880	3.630	2.465	3.430	2.420	3.450
5	**4f**	3.238	3.958	2.814	3.746	2.577	3.568
6	**6d**	1.961	1.670	1.932	1.862	1.523	1.503
7	**6e**	3.102	3.159	2.644	2.912	2.849	3.179
8	**6f**	0.848	0.604	0.046	0.000	0.000	0.000
9	Ratio of **2**:(**4** + **6**)	**5.4:1.0**	**2.8:1.0**	***1.8:1.0***	***1.0:1.3***	***1.1:1.0***	***1.0:1.7***

Table 6
Relative free energy magnitudes in solution by the B3LYP/6-311++G(d,p)//MP2/6-31+G(d) method using PCM model

Entry	Conf. no.	In methanol	In acetone	In chloroform
1	**2a**	0.505	0.024	0.000
2	**2b**	3.063	2.552	2.506
3	**2c**	0.000	0.000	0.006
4	**4d**	2.926	2.374	2.089
5	**4f**	3.259	2.703	2.219
6	**6d**	2.186	2.004	1.328
7	**6e**	3.462	2.844	2.784
8	**6f**	1.209	0.243	−0.077
9	Ratio of **2**:(**4** + **6**)	8.5:1	2.7:1	1.5:1

Table 7
Relative free energy magnitudes in solution by the MP2/6-311++G(d,p)//MP2/6-31+G(d) method using CPCM model

Entry	Conf. no.	In methanol	In acetone	In chloroform
3	**2a**	0.122	0.000	0.000
1	**2b**	2.561	2.398	2.371
2	**2c**	0.000	0.377	0.422
4	**4d**	3.016	2.801	2.525
5	**4f**	3.947	3.730	3.244
6	**6d**	2.834	3.022	2.366
7	**6e**	3.365	3.083	3.064
8	**6f**	1.748	1.095	0.789
9	Ratio of **2**:(**4** + **6**)	25.7:1	8.6:1	4.9:1

Table 8
The relative energy magnitudes by the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) level using B3LYP/6-31G(d)-optimized geometries via CPCM model (with energy in kcal/mol)

Entry	Conf. no.	ΔE in methanol		ΔE in acetone		ΔE in $CHCl_3$	
		B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
1	**2a**	2.308	2.975	2.047	2.713	2.510	3.162
2	**2b**	3.012	3.429	2.685	3.100	3.048	3.475
3	**2c**	0.000	0.000	0.000	0.000	0.000	0.000
4	**4d**	2.536	3.349	2.442	3.256	2.633	3.445
5	**4f**	3.762	4.564	3.363	4.161	3.802	4.101
6	**6d**	2.490	2.233	2.593	2.340	3.638	1.990
7	**6e**	2.595	2.685	2.46	2.550	2.435	2.521
8	**6f**	1.254	1.137	1.187	1.069	0.451	0.298
9	Ratio **2**:(**4** + **6**)	**6.3:1.0**	**5.5:1.0**	**5.8:1.0**	**5.1:1.0**	**2.0:1.0**	**3.1:1.0**

Table 9
The relative energy magnitudes by the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) methods using MP2/6-311+G(d)-optimized geometries via CPCM model (with energy in kcal/mol)

Entry	Conf. no.	ΔE in methanol		ΔE in acetone		ΔE in chloroform	
		B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
1	**2a**	0.367	0.601	0.000	0.44	0.205	0.693
2	**2b**	3.149	3.580	2.725	3.365	2.850	3.554
3	**2c**	0.00	0.00	0.127	0.352	0.379	0.665
4	**4d**	2.955	3.706	2.525	3.487	2.554	3.577
5	**4f**	3.339	4.060	2.910	3.839	2.795	3.782
6	**6d**	2.027	1.739	2.011	1.939	1.739	1.719
7	**6e**	3.109	3.166	2.592	2.855	2.721	3.045
8	**6f**	0.898	0.657	0.048	0.000	0.000	0.000
9	Ratio of **2**:(**4** + **6**)	3.8:1.0	3.5:1.0	1.8:1.0	1.0:1.0	1.1:1.0	1.0:1.7

isomers were 1.6:1, 1:9.5 and 1:2.4, using SPE in methanol, chloroform and acetone, respectively. These ratios were 1.5:1, 1:13.5 and 1:2.6, respectively, with the use of the total free energy in a solution. The fraction of **2** in a highly polar solvent is more than that in a low polar solvent. However, the faction of **2** in methanol was much smaller than those obtained in other methods, in which the ratio was from 3.5:1 to 34:1.

Table 10
Ratios of **2**:(**4** + **6**) in three solvents using total free energy in the solution through CPCM model used in four methods

Entry	Method	In MeOH	In $CHCl_3$	In MeCOMe
1	B3LYP//B3LYP	**8.5**:**1**	**1.5**:**1**	**2.7**:**1**
2	MP2//B3LYP	34.1:1	12.8:1	29.0:1
3	B3LYP//MP2	**9.2**:**1**	**1.6**:**1**	**2.8**:**1**
4	MP2//MP2	27.6:1	5.1:1	8.8:1

All methods provided different predictions of the ratios. However, all predictions pointed out that the higher the polarity of a solvent is, the greater the fractions of configurational isomer **2** are in the solvent. To determine this ratio, experimental ^{1}H NMR was tested. Compound **1** was used in ^{1}H NMR determinations in methanol, chloroform and acetone, respectively. The integration area was used in the ratio computations (Fig. 1). The ratios determined for two configurational isomers were 7.8:1, 1.7:1 and 4.5:1 in methanol, chloroform and acetone, respectively.

It was found that MP2/6-311++G(d,p)//B3LYP/6-31G(d) gave the most accurate estimation than B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) (Table 3), whereas B3LYP/6-311++G(d,p)//MP2/6-311+G(d) gave the worst estimation in the prediction of the ratios among all methods (Tables 2–5). Indeed, the computational time using MP2/6-311+G(d)-optimized geometries was much longer than that using B3LPY/6-31G(d). Thus, this method was expected to give more accurate predictions for configurations conformational distribution analyses than the other methods. However, MP2/6-311++G(d,P)//B3LYP/6-31G(d) method provided the most estimations in different solvents using PCM or CPCM models. The full optimization of the configurational and conformational isomers in the three different solvents did not predict unexpectedly the correct distributions of these isomers in the three solvents. It is therefore suggested that the simplified model used in place of the full molecule, might have caused that. Using the whole molecule as the computational target via MP2/6-311+G(d) should be much time-consuming. A rather better strategy would be using a reasonable simplified model and suitable computational method which would provide a useful tool in the conformation analyses for organic research.

Finally, the ratio of different configurational isomers of **2**, **4** and **6** in water was investigated using B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) and MP2/6-311++G(d,p)//B3LYP/6-31G(d) methods via CPCM models, respectively. The computed ratios were 7.8:1 and 6.3:1, respectively. The fraction of **2** in water was greater than that in methanol (6.3:1 and 5.5:1, respectively, Table 8, entry 8) using the same method. The more polar the solvent is, the higher the ratio of two configurational isomers will be in that solvent.

4. Summary

Distribution analysis of configurational and conformational isomers of 1α,7α-diacetoxyl-17α-20*S*-21,24-epoxy-apo-tirucall-14-ene-3α,23*R*,24*S*,25-tetraol in different solutions was performed using the simplified model **2**. The computational methods used were B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) or MP2/6-311++G(d,p)//B3LYP/6-31G(d) integrated with PCM or CPCM models.

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