Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

ANALYSIS OF THYME ESSENTIAL OILS USING GAS-PHASE BROADBAND ROTATIONAL SPECTROSCOPY

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Figure S1. Experimental (black color) and simulated (blue) broadband rotational spectrum of linalool in the 2-18 GHz spectral region.

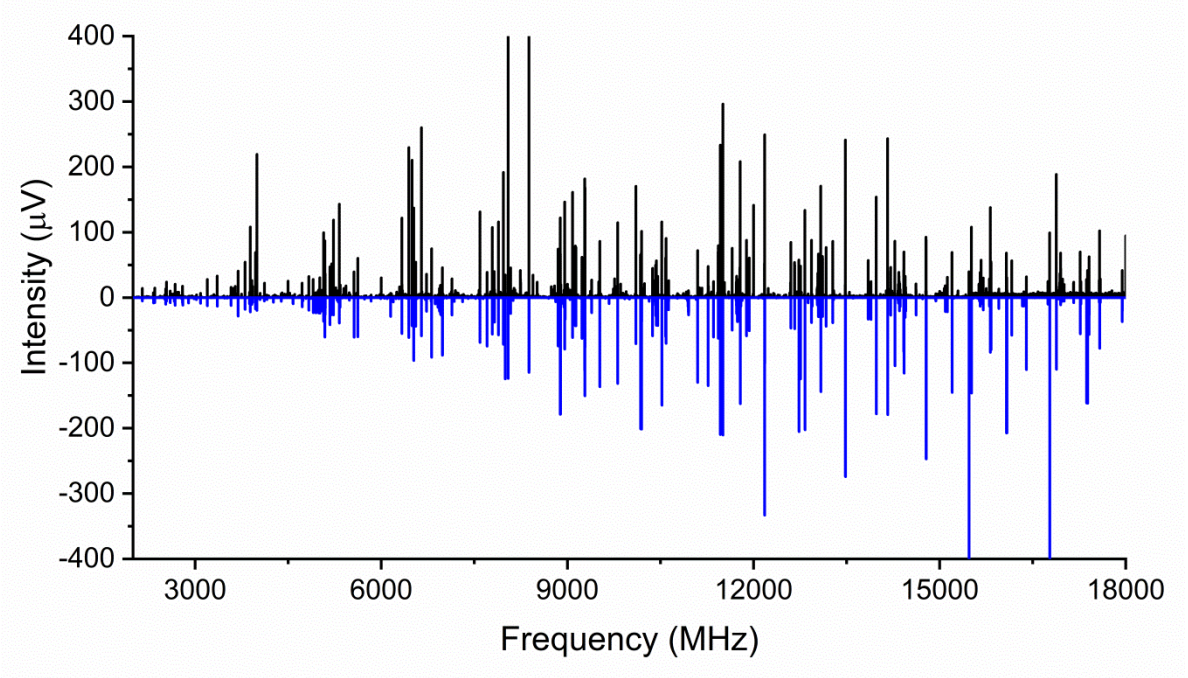

Table S1. Vapor pressures of the terpenes identified at different temperatures. The temperatures studied in this work have been marked in red.

Terpenes	Vapor pressure (mmHg)	Vapor pressure (mmHg)	Vapor pressure (mmHg)	Vapor pressure (mmHg)	Vapor pressure (mmHg)	Vapor pressure (mmHg)
	1	5	10	20	40	60
	Temperature (ºC)					
Thymol[a]	64.3	92.8	107.4	122.6	139.8	149.8
Carvacrol[a]	70.0	98	113	128	145.2	155.3
4-carvomenthenol[a]	52.8	80.4	94.3	109.8	126.0	136.3
Camphor[a]	41.5	68.6	82.3	97.5	114.0	124.0
Linalool[b,c]	48.0[b]	69.7[b]	79.9[b]	95.2[c]	109.4[c]	125.7[c]

[a] Vapor pressures taken from "Perry's Chemical Engineers' Handbook, Eds.: R. H. Perry, D. W. Green, J. O. Maloney, McGraw-Hill, 1997".

[b] Vapor pressures taken from "D. H. Zaitsau, S. P. Verevkin, A. Y. Sazonova, *Fluid Ph. Equilibria* 2015, **386,** 140–148", at 1.1, 4.7 and 8.5 mmHg instead of 1, 5 and 10 mmHg, respectively.

[c] Vapor pressures taken from "R. A. Clará, A. C. G. Marigliano, H. N. Sólimo, *J. Chem. Eng. Data*, 2009, **54**, 1087-1090" at 18.8, 37.5, and 75 mmHg instead of 20, 40 and 60 mmHg, respectively.

Table S2. Vapor pressures of the terpenes identified at 25 ºC.

Terpenes	Vapor pressure at 25 ºC (mmHg)
thymol	0.016[a]
carvacrol	0.03[b]
linalool	0.15[c]
4-carvomenthenol	0.04[d]
camphor	0.65[a]

[a] Taken from reference A. H. Jones *J. Chem. Eng. Data* 1960, **5**, 196-200.
[b] Taken from Parchem company
[c] Taken from ILO International Chemical Safety Cards (ICSC)
[d] Taken from US EPA; Estimation Program Interface (EPI) Suite. Ver. 4.1. Nov, 2012

Table S3. For the given *a*-type transitions 4_{14}-3_{13}, 4_{04}-3_{03} and 4_{13}-3_{12}, we provide the intensities and the intensity/μ_a^2 ratios for the different conformers found in **thyme I** and **thyme II** essential oils. In the case of camphor, the analysis has been done with the *a*-type transitions 2_{12}-1_{11}, 2_{02}-1_{01} and 2_{11}-1_{10}. The labeling of the rotational transitions follows the $J_{K_aK_c}$ scheme.

THYME I						
Transitions	**Intensity (μV)**	**I/μ_a^2 (μV/D^2)**	**Intensity (μV)**	**I/μ_a^2 (μV/D^2)**	**Intensity (μV)**	**I/μ_a^2 (μV/D^2)**
	***trans*-thymol-A**		***trans*-thymol-B**		***cis*-thymol-A**	
4_{14}-3_{13}	272	133.01	39	17.33	33	24.95
4_{04}-3_{03}	286	139.86	59	26.22	40	30.25
4_{13}-3_{12}	269	131.55	12	5.33	30	22.68
	***trans*-carvacrol-A**		***trans*-carvacrol-B**		***cis*-carvacrol-A**	
4_{14}-3_{13}	10	6.10	10	4.96	4	6.75
4_{04}-3_{03}	11	6.71	9	4.46	7	11.81
4_{13}-3_{12}	13	7.93	5	2.48	6	10.12
	***cis*-carvacrol-B**		**linalool**		**4-carvomenthenol A**	
4_{14}-3_{13}	9	8.16	5	4.00	2	1.04
4_{04}-3_{03}	4	3.63	4	3.20	3	1.55
4_{13}-3_{12}	5	4.54	8	6.40	1	0.52
	4-carvomenthenol B		**4-carvomenthenol C**			
4_{14}-3_{13}	2	1.32	4	3.02		
4_{04}-3_{03}	1	0.66	3	2.27		
4_{13}-3_{12}	-	-	1	0.76		
	camphor		***trans*-thymol-A**			
2_{12}-1_{11}	6	0.67	63	30.81		
2_{02}-1_{01}	4	0.45	30	14.67		
2_{11}-1_{10}	11	1.23	29	14.18		

THYME II						
Transitions	**Intensity (μV)**	**I/μ_a^2 (μV/D^2)**	**Intensity (μV)**	**I/μ_a^2 (μV/D^2)**	**Intensity (μV)**	**I/μ_a^2 (μV/D^2)**
	***trans*-thymol-A**		**linalool**		**4-carvomenthenol A**	
4_{14}-3_{13}	2	0.98	54	43.20	36	18.63
4_{04}-3_{03}	7	3.42	45	36.00	42	21.74
4_{13}-3_{12}	2	0.98	78	62.40	20	10.35
	4-carvomenthenol B		**4-carvomenthenol C**			
4_{14}-3_{13}	19	12.56	60	45.37		
4_{04}-3_{03}	24	15.86	37	27.98		
4_{13}-3_{12}	6	3.97	30	22.68		
	camphor		**linalool**			
2_{12}-1_{11}	1	0.11	7	5.60		
2_{02}-1_{01}	1	0.11	5	4.00		
2_{11}-1_{10}	3	0.33	5	4.00		

Table S4. For the different conformers identified in **thyme I** and **thyme II** oils, we provide the corresponding intensity/μ_a^2 values and the μ_a^2 ones, as well as their corresponding errors. See text below for the explanation of the errors calculation.

THYME I				
	$\mu_a^2 \pm$ Error[a]	**$I/\mu_a^2 \pm$ Error[b] of the different transitions**		
Conformer		**4_{14}-3_{13}**	**4_{04}-3_{03}**	**4_{13}-3_{12}**
trans-thymol-A	2.04 ± 0.41	133.01 ± 26.61	139.86 ± 27.98	131.55 ± 26.31
trans-thymol-B	2.25 ± 0.45	17.33 ± 3.50	26.22 ± 5.26	5.33 ± 1.16
cis-thymol-A	1.32 ± 0.26	24.95 ± 5.05	30.25 ± 6.10	22.68 ± 4.60
trans-carvacrol-A	1.64 ± 0.33	6.10 ± 1.36	6.71 ± 1.47	7.93 ± 1.70
trans-carvacrol-B	2.02 ± 0.40	4.96 ± 1.11	4.46 ± 1.02	2.48 ± 0.70
cis-carvacrol-A	0.59 ± 0.12	6.75 ± 2.16	11.81 ± 2.90	10.12 ± 2.63
cis-carvacrol-B	1.10 ± 0.22	8.16 ± 1.87	3.63 ± 1.16	4.54 ± 1.28
linalool	1.25 ± 0.25	4.00 ± 1.13	3.20 ± 1.02	6.40 ± 1.51
4-carvomenthenol A	1.93 ± 0.39	1.04 ± 0.56	1.55 ± 0.60	0.52 ± 0.53[d]
4-carvomenthenol B	1.51 ± 0.30	1.32 ± 0.71	0.66 ± 0.67[d]	-
4-carvomenthenol C	1.32 ± 0.26	3.02 ± 0.97	2.27 ± 0.88	0.76 ± 0.77[d]
camphor	8.96 ± 0.01	0.67 ± 0.11[c]	0.45 ± 0.11[c]	1.23 ± 0.11[c]
THYME II				
	$\mu_a^2 \pm$ Error[a]	**$I/\mu_a^2 \pm$ Error[b] of the different transitions**		
Conformer		**4_{14}-3_{13}**	**4_{04}-3_{03}**	**4_{13}-3_{12}**
trans-thymol-A	2.04 ± 0.41	0.98 ± 0.53	3.42 ± 0.84	0.98 ± 0.53
linalool	1.25 ± 0.25	43.20 ± 8.68	36.00 ± 7.24	62.40 ± 12.51
4-carvomenthenol A	1.93 ± 0.39	18.63 ± 3.76	21.74 ± 4.38	10.35 ± 2.13
4-carvomenthenol B	1.51 ± 0.30	12.56 ± 2.60	15.86 ± 3.24	3.97 ± 1.03
4-carvomenthenol C	1.32 ± 0.26	45.37 ± 9.11	27.98 ± 5.65	22.68 ± 4.60
camphor	8.96 ± 0.01	0.11 ± 0.11[c,d]	0.11 ± 0.11[c,d]	0.33 ± 0.11[c]

[a] $(z \pm \Delta z)^2 = y \pm \Delta y$

[b] $\frac{(x \pm \Delta x)}{(y \pm \Delta y)}$

[c] *For camphor, the transitions analyzed are 2_{12}-1_{11}, 2_{02}-1_{01} and 2_{11}-1_{10}, instead of 4_{14}-3_{13}, 4_{04}-3_{03} and 4_{13}-3_{12}.*

[d] *Large errors because the intensity values are 1 μV, and we consider the error in the intensity to be 1 μV (see explanation below).*

- **I ± Error** $(x \pm \Delta x)$

Here x is the intensity value of the different transitions. We consider Δx to be twice the noise level of the spectra, which was 0.5 μV in both oils, that is, $\Delta x = 1\ \mu V$.

- **μ_a^2 ± Error** $(z \pm \Delta z)^2 = y \pm \Delta y$

z is μ_a. We calculated the error of the square of the dipole moment component using the following error propagation formula:

$$f = (z \pm \Delta z)^m = z^m \pm z^m \left(\frac{m\Delta z}{z}\right)$$

In our case, $m = 2$,

$$f = (z \pm \Delta z)^2 = z^2 \pm z^2 \left(\frac{2\Delta z}{z}\right)$$

We consider $\Delta z = 0.1 \times z$, because we consider the error in the estimation of the theoretical dipole moment components to be 10%. For camphor, we take into account the experimental μ_a value determined from Stark effect measurements and its corresponding error (0.9934 (23) D, *Phys. Chem. Chem. Phys.*, **2003**, *5*, 820–826).

For example, for the 4_{14}-3_{13} transition of the conformer *trans*-thymol-A in thyme I oil:

$$f = (1.43 \pm 0.14)^2 = 1.43^2 \pm 1.43^2 \left(\frac{2 \times 0.14}{1.43}\right)$$

$$f = 2.04 \pm 0.41$$

We also consider $y = z^2$ for the following calculations, then:

$$f = (z \pm \Delta z)^2 = z^2 \pm z^2 \left(\frac{2\Delta z}{z}\right) = y \pm \Delta y = 2.04 \pm 0.41$$

- **$I/\mu_a^2 \pm$ Error $\frac{(x \pm \Delta x)}{(y \pm \Delta y)}$**

For the error calculation of the I/μ_a^2 values, we have used the following error propagation formula:

$$f = \frac{(x \pm \Delta x)}{(y \pm \Delta y)} = \left(\frac{x}{y}\right) \pm \left(\frac{x}{y}\right) \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2}$$

Where x is the intensity of the transition, Δx is 1 μV (twice the noise level), y is μ_a^2, and Δy is the error of the square of the *a* dipole moment component.

As an example, for the 4_{14}-3_{13} transition of the conformer *trans*-thymol-A in thyme I oil:

$$f = \frac{(272 \pm 1)}{(2.04 \pm 0.41)} = \left(\frac{272}{2.04}\right) \pm \left(\frac{272}{2.04}\right) \sqrt{\left(\frac{1}{272}\right)^2 + \left(\frac{0.41}{2.04}\right)^2}$$

$$f = 133.01 \pm 26.61$$

As mentioned in section 3.1. of the manuscript, several conformers in these oils present methyl group internal rotation, resulting in line splittings into two or more components, so that the sum of the intensities needs to be taken. For the ones that were weak or whose splittings could not be resolved, we used the XIAM program to predict the magnitude of the respective splitting.

Table S5. Normalization of the I/μ_a^2 values obtained in Table S1 for each conformer with respect to *trans*-thymol-A or linalool in the cases of **thyme I** or **thyme II** oils, respectively, and their corresponding errors.

THYME I

Transitions	*trans*-thymol-A / *trans*-thymol-A	Error[a]	*trans*-thymol-B / *trans*-thymol-A	Error	*cis*-thymol-A / *trans*-thymol-A	Error
4_{14}-3_{13}	1.00	0.20	0.13	0.03	0.19	0.04
4_{04}-3_{03}	1.00	0.20	0.19	0.04	0.22	0.04
4_{13}-3_{12}	1.00	0.20	0.04	0.01	0.17	0.03
Average	1.00	0.20	0.12	0.02	0.19	0.04
Transitions	***trans*-carvacrol-A / *trans*-thymol-A**	**Error**	***trans*-carvacrol-B / *trans*-thymol-A**	**Error**	***cis*-carvacrol-A / *trans*-thymol-A**	**Error**
4_{14}-3_{13}	0.05	0.01	0.04	0.008	0.05	0.02
4_{04}-3_{03}	0.05	0.01	0.03	0.007	0.08	0.02
4_{13}-3_{12}	0.06	0.01	0.02	0.005	0.08	0.02
Average	0.05	0.01	0.03	0.007	0.07	0.02
Transitions	***cis*-carvacrol-B / *trans*-thymol-A**	**Error**	**linalool / *trans*-thymol-A**	**Error**	**4-carvomenthenol A / *trans*-thymol-A**	**Error**
4_{14}-3_{13}	0.06	0.01	0.03	0.01	0.008	0.004
4_{04}-3_{03}	0.03	0.01	0.02	0.01	0.011	0.004
4_{13}-3_{12}	0.03	0.01	0.05	0.01	0.004	0.004
Average	0.04	0.01	0.03	0.01	0.008	0.004
Transitions	**4-carvomenthenol B / *trans*-thymol-A**	**Error**	**4-carvomenthenol C / *trans*-thymol-A**	**Error**		
4_{14}-3_{13}	0.010	0.005	0.02	0.007		
4_{04}-3_{03}	0.005	0.005	0.02	0.006		
4_{13}-3_{12}	-	-	0.01	0.006		
Average	0.007	0.005	0.02	0.006		
Transitions	**camphor / *trans*-thymol-A**	**Error**				
2_{12}-1_{11}	0.02	0.004				
2_{02}-1_{01}	0.03	0.008				
2_{11}-1_{10}	0.09	0.008				
Average	0.05	0.006				

THYME II

Transitions	linalool/ linalool	Error[a]	*trans*-thymol-A / linalool	Error	4-carvomenthenol A / linalool	Error
4_{14}-3_{13}	1.00	0.20	0.02	0.01	0.43	0.09
4_{04}-3_{03}	1.00	0.20	0.10	0.02	0.60	0.12
4_{13}-3_{12}	1.00	0.20	0.02	0.01	0.17	0.03
Average	1.00	0.20	0.04	0.01	0.40	0.08
Transitions	**4-carvomenthenol B / linalool**	**Error**	**4-carvomenthenol C / linalool**	**Error**		
4_{14}-3_{13}	0.29	0.06	1.05	0.21		
4_{04}-3_{03}	0.44	0.09	0.78	0.16		
4_{13}-3_{12}	0.06	0.02	0.36	0.07		
Average	0.26	0.06	0.73	0.15		
Transitions	**camphor / linalool**	**Error**				
2_{12}-1_{11}	0.02	0.02				
2_{02}-1_{01}	0.03	0.02				
2_{11}-1_{10}	0.08	0.02				
Average	0.04	0.02				

[a] Error of the I/μ_a^2 values ($\frac{\Delta x}{\Delta y}$, see Table S2) divided by the I/μ_a^2 values obtained in Table S1 for each conformer with respect to *trans*-thymol-A or linalool in the cases of **thyme I** or **thyme II** oils, respectively.

Table S6. Percentages of the different terpenes identified by Florihana (gas chromatography analysis) and their normalization with respect to the most stable ones (thymol for **thyme I** oil and linalool for **thyme II**) to obtain the corresponding ratios.

THYME I			**THYME II**		
Lot number B221217ES			**Lot number B280917ES**		
Terpene	**Percentage obtained by Florihana**	**Ratios**	**Terpene**	**Percentage obtained by Florihana**	**Ratios**
thymol	34.7	1.00	linalool	30.4	1.00
carvacrol	3.5	0.10	*trans*-thymol-A	0.3	0.01
linalool	5.4	0.16	camphor	0.8	0.03
4-carvomenthenol	1.0	0.03	4-carvomenthenol	14.1	0.46
camphor	2.6	0.07			
Lot number L121018ES			**Lot number L280818ES**		
Terpene	**Percentage obtained by Florihana**	**Ratios**	**Terpene**	**Percentage obtained by Florihana**	**Ratios**
thymol	37.3	1.00	linalool	32.1	1.00
carvacrol	3.2	0.09	*trans*-thymol-A	0.5	0.02
linalool	4.9	0.13	camphor[b]	<9.2	<0.28
4-carvomenthenol[a]	<12.1	<0.30	4-carvomenthenol	14.2	0.44
camphor[a]	<12.1	<0.30			
			Lot number B230419ES		
			Terpene	**Percentage obtained by Florihana**	**Ratios**
			linalool	45.1	1.00
			trans-thymol-A	0.4	0.01
			camphor	0.6	0.01
			4-carvomenthenol	8.6	0.19

These percentages can be found on the supplier's webpage (https://www.florihana.com/en/90-essential-oils).

[a] Percentages not specified by the supplier. They provide 87.9 % of the components for lot number **L121018ES**. Thus, in the case that 4-carvomenthenol and camphor could be present they would be in a significantly lower amount than 12.1%, that is, a ratio lower than 0.30.

[b] Percentage not specified by the supplier. They provide 90.8 % of the components for lot number **L280818ES**. Thus, in the case that camphor could be present it would be in a significantly lower amount than 9.2%, that is, a ratio lower than 0.28.

Table S7. Experimental spectroscopic constants for the singly substituted ^{13}C species of *trans*-thymol-A.

	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$
A / MHz	2047.4951(82)	2048.256(65)	2055.449(41)	2039.283(32)
B / MHz	739.13783(78)	736.5987(13)	733.88943(84)	736.85042(60)
C / MHz	590.83356(50)	589.2441(10)	588.09237(70)	588.65962(62)
N[a]	16	10	13	12
σ[b] / kHz	7.22	8.63	5.85	4.58

	$^{13}C_5$	$^{13}C_6$	$^{13}C_7$	$^{13}C_8$
A / MHz	2040.516(88)	2055.658(41)	2055.692(46)	2042.70280(85)
B / MHz	739.1859(26)	738.78814(60)	734.3329 (11)	730.14210(38)
C / MHz	590.2372(17)	591.27520(57)	588.44167(79)	586.63359(25)
N[a]	7	10	10	5
σ[b] / kHz	7.89	4.43	5.45	1.10

	$^{13}C_9$	$^{13}C_{10}$
A / MHz	2037.441(41)	2055.130(34)
B / MHz	730.37175(78)	724.46602(56)
C / MHz	584.90937(73)	582.02802(60)
N[a]	12	11
σ[b] / kHz	5.40	4.35

[a]Number of the fitted transitions
[b]Standard deviation of the fit

Table S8. Experimental spectroscopic constants for the singly substituted ^{13}C species of linalool (conformer I).

	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$
A / MHz	1646.4221(21)	1634.7710(14)	1632.25(18)	1642.9206(36)
B / MHz	679.64186(50)	680.57096(66)	680.5122(14)	673.28321(70)
C / MHz	616.62645(61)	616.60856(62)	617.9447(11)	611.36498(96)
N[a]	18	17	14	11
σ[b] / kHz	9.2	7.9	8.5	9.6

	$^{13}C_5$	$^{13}C_6$	$^{13}C_7$	$^{13}C_8$
A / MHz	1638.6873(35)	1640.4013(31)	1646.8114(48)	1639.9475(21)
B / MHz	679.27907(61)	680.3364(11)	677.40273(95)	671.10972(70)
C / MHz	615.6117(10)	616.49375(83)	614.80495(80)	610.41089(71)
N[a]	15	13	11	17
σ[b] / kHz	8.3	7.8	7.0	9.1

	$^{13}C_9$	$^{13}C_{10}$
A / MHz	1636.0335(29)	1620.0631(35)
B / MHz	676.77637(93)	680.88714(72)
C / MHz	613.33782(56)	613.86295(74)
N[a]	17	12
σ[b] / kHz	8.0	7.1

[a]Number of the fitted transitions
[b]Standard deviation of the fit

Table S9. Comparison of the *a*, *b* and *c* coordinates of the r_s, r_0 and r_e (MP2/6-311++G(d,p)) structures for *trans*-thymol-A. All the coordinates are given in Å.

	atom	*a*	*b*	*c*
r_s		0.103(15)	0.9963(16)	-0.1763(88)
r_0	C1	0.146(31)	0.992(17)	-0.1790(49)
r_e		0.193	1.029	-0.204
r_s		1.5464(16)	0.9627(26)	-0.099(25)
r_0	C2	1.5619(98)	0.955(19)	-0.0936(61)
r_e		1.588	0.966	-0.131
r_s		2.22311(89)	-0.2477(80)	0.068(29)
r_0	C3	2.2319(61)	-0.2471(99)	0.0547(29)
r_e		2.248	-0.259	0.047
r_s		1.4668(12)	-1.4216(13)	0.099(18)
r_0	C4	1.4834(96)	-1.416(12)	0.0869(90)
r_e		1.470	-1.422	0.119
r_s		0.0399 *i* [a]	-1.3682(23)	0.0382 *i* [a]
r_0	C5	0.096(29)	-1.370(10)	0.004(16)
r_e		0.073	-1.352	0.038
r_s		-0.5867(33)	-0.135(15)	-0.149(13)
r_0	C6	-0.614(25)	-0.131(16)	-0.157(13)
r_e		-0.598	-0.134	-0.138
r_s		-2.11960(98)	-0.0347 *i* [a]	-0.194(11)
r_0	C7	-2.1271(68)	-0.037(14)	-0.215 (21)
r_e		-2.106	-0.013	-0.186
r_s		-2.64562(57)	0.3609(42)	1.2220(12)
r_0	C8	-2.6663(52)	0.298(20)	1.1797(66)
r_e		-2.638	0.371	1.204
r_s		-2.79723(71)	-1.3643(15)	-0.6500(31)
r_0	C9	-2.8093(57)	-1.366(14)	-0.605(25)
r_e		-2.797	-1.279	-0.699
r_s		3.72908(49)	-0.2838(65)	0.161(11)
r_0	C10	3.7343(36)	-0.274(15)	0.188(11)
r_e		3.751	-0.308	0.168

[a] Imaginary coordinate.

Table S10. Comparison of the *a*, *b* and *c* coordinates of the r_s, r_0 and r_e (MP2/6-311++G(d,p)) structures for linalool (conformer I). All the coordinates are given in Å.

	atom	*a*	*b*	*c*
r_s		-1.66767(92)	-0.2086(74)	0.124(12)
r_0	C1	-1.6639(66)	-0.2077(65)	0.174(12)
r_e		-1.650	-0.192	0.171
r_s		-1.0868(14)	-1.2858(12)	-0.7783(20)
r_0	C2	-1.094(15)	-1.277(10)	-0.793(15)
r_e		-1.118	-1.308	-0.747
r_s		0.300(28)	-0.9788(86)	-1.3324(65)
r_0	C3	0.333(24)	-0.998(12)	-1.333(11)
r_e		0.293	-1.071	-1.315
r_s		-3.08205(51)	-0.6273(25)	0.5795(27)
r_0	C4	-3.0921(44)	-0.560(15)	0.567(18)
r_e		-3.095	-0.496	0.567
r_s		-1.70928(92)	1.1191(14)	-0.5191(30)
r_0	C5	-1.7081(90)	1.133(12)	-0.509(10)
r_e		-1.600	1.134	-0.553
r_s		1.3853(12)	-1.0396(15)	-0.3364(47)
r_0	C6	1.399(11)	-1.017(14)	-0.330(20)
r_e		1.361	-1.066	-0.256
r_s		2.29539(69)	-0.0904 i [a]	0.0792 i [a]
r_0	C7	2.2973(59)	-0.0389(80)	0.0208(67)
r_e		2.248	-0.087	0.032
r_s		3.32764(47)	-0.3101(50)	1.0982(14)
r_0	C8	3.3310(46)	-0.295(16)	1.099(15)
r_e		3.260	-0.271	1.135
r_s		2.35840(66)	1.2880(12)	-0.6164(25)
r_0	C9	2.3609(62)	1.295(11)	-0.606(23)
r_e		2.345	1.229	-0.694
r_s		-1.1951(13)	2.25802(69)	-0.1155 i [a]
r_0	C10	-1.203(10)	2.2595(63)	-0.011(20)
r_e		-1.057	2.258	-0.061

[a] Imaginary coordinate.

Table S11. The r_0, r_s and r_e (MP2 and B3LYP-D3) structures for *trans*-thymol-A.

	r_0	r_s	r_e [a]	r_e [b]
r(C1-O1) / Å	1.394(42)	-	1.38	1.38
r(C1-C2) / Å	1.419(35)	1.446(15)	1.40	1.39
r(C2-C3) / Å	1.384(23)	1.3968(87)	1.40	1.40
r(C3-C4) / Å	1.389 (17)	1.3968(69)	1.40	1.39
r(C4-C5) / Å	1.391(30)	*1.4711(18)*[c]	1.40	1.40
r(C5-C6) / Å	1.437(32)	*1.374(13)*	1.40	1.39
r(C3-C10) / Å	1.5085(74)	1.5093(22)	1.51	1.51
r(C6-C7) / Å	1.518(26)	*1.5395(37)*	1.51	1.52
r(C7-C8) / Å	1.533(25)	*1.5530(99)*	1.54	1.54
r(C7-C9) / Å	1.544(19)	*1.5901(35)*	1.53	1.53
≤(C1-C2-C3) / °	121(1)	120.67(27)	121.0	121.0
≤(C2-C3-C4) / °	118.22(67)	117.94(25)	118.1	118.0
≤(C2-C3-C10) / °	[120.5][d]	120.77(54)	120.5	120.4
≤(C3-C4-C5) / °	120.55(76)	*120.52(27)*	120.6	120.6
≤(C4-C3-C10) / °	[121.5]	121.25(57)	121.5	121.6
≤(C4-C5-C6) / °	[121.9]	*117.75(33)*	121.9	122.2
≤(C5-C6-C7) / °	[123.4]	*120.46(81)*	123.4	123.5
≤(C5-C6-C1) / °	[117.0]	*123.11(62)*	117.0	116.7
≤(C6-C1-C2) / °	[121.4]	119.92(66)	121.4	121.5
≤(C6-C7-C8) / °	109.24(75)	*109.32(73)*	109.6	110.3
≤(C6-C7-C9) / °	113.41(83)	*110.96(56)*	113.3	113.6
≤(C8-C7-C9) / °	[110.7]	*108.45(37)*	110.7	110.7
≤(C1-C2-C3-C10) / °	[-178.1]	-179(2)	-178.1	-179.6
≤(C10-C3-C4-C5) / °	[178.4]	*-180(2)*	178.4	179.7
≤(C4-C5-C6-C7) / °	[-178.0]	*-177(1)*	-178.0	-178.4
≤(C5-C6-C7-C8) / °	[96.2]	*96.14(95)*	96.2	99.7
≤(C5-C6-C7-C9) / °	-21(2)	*-23(1)*	-28.0	-25.2
≤(C1-C6-C7-C8) / °	[-80.5]	*-80(1)*	-80.5	-78.6
≤(C1-C6-C7-C9) / °	[155.3]	*160.62(90)*	155.3	156.4
≤(C6-C7-C8-C9) / °	[-125.7]	*-121.10(67)*	-125.7	-126.6

[a] Structure calculated at the MP2/6-311++G(d,p) level of theory.

[b] Structure calculated at the B3LYP-D3/6-311++G(d,p) level of theory.

[c] The structural parameters involving C5 and C7 atoms (in italics) have been calculated by setting the imaginary r_s coordinates to zero.

[d] Values kept fixed to *ab initio* (MP2) theoretical structure.

Table S12. The r_0, r_s and r_e (MP2 and B3LYP-D3) structures for linalool (conformer I).

	r_0	r_s	r_e[a]	r_e[b]
r(C1-O1) / Å	1.440(32)	-	1.43	1.43
r(C1-C2) / Å	1.550(21)	1.5205(92)	1.54	1.55
r(C1-C5) / Å	1.505(16)	1.4758(88)	1.51	1.52
r(C1-C4) / Å	1.5227(98)	1.5438(44)	1.53	1.53
r(C5-C10) / Å	1.332(16)	*1.3531(19)*[c]	1.34	1.33
r(C2-C3) / Å	1.551(29)	1.524(26)	1.54	1.54
r(C3-C6) / Å	1.464(35)	1.475(22)	1.50	1.50
r(C6-C7) / Å	1.374(20)	*1.4220(18)*	1.35	1.34
r(C7-C8) / Å	1.515(11)	*1.5388(15)*	1.51	1.51
r(C7-C9) / Å	1.475(16)	*1.4293(15)*	1.51	1.51
≤(C2-C1-O1) / °	107.57(99)	-	110.9	110.9
≤(C4-C1-O1) / °	[105.1][d]	-	105.1	105.3
≤(C5-C1-O1) / °	117(1)	-	111.9	111.7
≤(C1-C5-C10) / °	[124.9]	*125.40(44)*	124.9	125.5
≤(C4-C1-C5) / °	[109.3]	110.29(29)	109.3	109.2
≤(C4-C1-C2) / °	[109.7]	109.45(44)	109.7	109.7
≤(C1-C2-C3) / °	115.56(73)	114.87(36)	115.2	115.5
≤(C2-C3-C6)/ °	115.39(61)	114.57(55)	113.0	113.9
≤(C3-C6-C7) / °	130(1)	*126.93(46)*	128.2	128.5
≤(C6-C7-C8) / °	[120.5]	*116.80(22)*	120.5	120.7
≤(C6-C7-C9) / °	124.33(80)	*125.80(16)*	124.9	124.8
≤(C5-C1-C2) / °	[109.8]	112.92(75)	109.8	109.9
≤(C8-C7-C9) / °	[114.6]	*117.38(18)*	114.6	114.5
≤(C3-C2-C1-O1) / °	[-69.0]	-	-69.0	-67.0
≤(C4-C1-O1-C2) / °	117.48(83)	-	118.5	118.6
≤(C5-C1-O1-C4) / °	[118.5]	-	118.5	118.4
≤(C10-C5-C1-C4) / °	[110.0]	*110.07(49)*	110.0	111.7
≤(C10-C5-C1-C2) / °	[-129.6]	*-127.12(45)*	-129.6	-128.0
≤(C1-C2-C3-C6) / °	[65.6]	71.25(84)	65.6	66.8
≤(C4-C1-C2-C3) / °	[175.3]	178.40(68)	175.3	177.0
≤(C2-C3-C6-C7) / °	-121.85(86)	*-122.77(57)*	-122.9	-122.2
≤(C3-C6-C7-C8) / °	[-179.6]	*178.95(94)*	-179.6	-179.6
≤(C6-C7-C8-C9) / °	[179.0]	*178.29(20)*	179.0	179.6

[a] Structure calculated at the MP2/6-311++G(d,p) level of theory.

[b] Structure calculated at the B3LYP-D3/6-311++G(d,p) level of theory.

[c] The structural parameters involving C10 and C7 atoms (in italics) have been calculated by setting the imaginary r_s coordinates to zero.

[d] Values kept fixed to *ab initio* (MP2) theoretical structure.

Table S13. Experimental and calculated (MP2/6-311++G(d,p) level of theory) molecular parameters for linalool. This fit includes only AA states due to internal rotation.

Parameter	Experimental	MP2/6-311++G(d,p)
A / MHz	1646.7350(12)	1637.70
B / MHz	682.19967(55)	700.36
C / MHz	618.75230(55)	635.51
Δ_J / kHz	0.0928(57)	0.11
Δ_K / kHz	0.505(38)	-0.29
σ^a / kHz	19.7	
N^b	83	

[a]Standard deviation of the fit
[b]Number of the fitted transitions

Table S14. Experimental and calculated molecular parameters for linalool obtained using XIAM to provide a global fit of all the internal rotation splittings, and quantum chemical calculations (B3LYP-D3 and MP2). Experimental molecular parameters obtained in ref. 10 are also included for comparison.

Parameter	Experimental	Experimental (ref. 10)	MP2/ 6-311++G(d,p)	B3LYP-D3 /6-311++G(d,p)
A / MHz	1646.73610(25)	1646.74020(46)	1637.70	1639.33
B / MHz	682.19743(15)	682.19862(16)	700.36	692.66
C / MHz	618.75028(19)	618.75100(20)	635.51	627.03
Δ_J / kHz	0.09988(75)	0.11550(54)	0.11	0.09
Δ_{JK} / kHz	0.4012(35)	0.3843(36)	0.44	0.30
Δ_K / kHz	-0.2846(58)		-0.29	-0.16
δ_J / kHz	-0.02134(92)	0.00735(32)	0.005	0.005
δ_K/ kHz		0.234(20)	0.25	0.18
k^a	-0.88	-0.88	-0.87	-0.87
$V_3(1)$ / kJ · mol^{-1}	4.7703(96)	4.7876(77)	3.9	
$V_3(2)$ / kJ · mol^{-1}	9.2581(74)		9.3	
I_α (1,2) / u Å^2	3.1586[b]	3.1586[b]		
≤δ(1) / rad	1.48572(85)		1.48420	
≤δ(2) / rad	[1.40500][c]		1.40500	
≤ε(1) / rad	0.440(11)		0.517	
≤ε(2) / rad	[0.836][c]		0.836	
≤(*i*,*a*) (1) / °	85.126(49)	85.04(10)	85.04	
≤(*i*,*b*) (1) / °	25.63(65)	30.01(39)	30.01	
≤(*i*,*c*) (1) / °	64.90(65)	60.49(38)	60.48	
≤(*i*,*a*) (2) / °	[47.88][c]		47.88	
≤(*i*,*b*) (2) / °	[82.97][c]		82.97	
≤(*i*,*c*) (2) / °	[42.98][c]		42.98	
σ[d] / kHz	10.8	4.6		
N[e]	384	83		
AA/AE/EA/EE$^+$ /EE$^-$ [f]	168/31/126/29/30			
A/E [g]		46/37		

[a] Ray's asymmetry parameter : $\frac{2B-A-C}{A-C}$

[b] Moment of inertia of the internal rotors, set to the value corresponding to F_0 = 160 GHz (a typical value for a methyl group)

[c] Fixed to the calculated value

[d] Standard deviation of the fit

[e] Number of the fitted transitions

[f] Number of the fitted AA/AE/EA/EE$^+$/EE$^-$ transitions.

[g] Number of the fitted A/E transitions.

Table S15. Observed rotational transitions (ν_{obs}) and the residuals (ν_{obs} - ν_{calc}) for linalool (conformer I), for the global XIAM fit.

J'	K_a'	K_c'	←	J''	K_a''	K_c''	State	$\nu_{obs} - \nu_{calc}$ (MHz)	ν_{obs} (GHz)
7	2	6		7	1	6	AA	-.0186	2.1491649
							EA	-.0113	2.1492959
1	1	0		0	0	0	AA	-.0187	2.3289212
6	2	5		6	1	5	AA	-.0062	2.3491437
							EA	-.0050	2.3492381
4	1	3		3	2	1	AA	-.0048	2.5089019
							EA	.0060	2.5087906
5	2	4		5	1	4	AA	-.0032	2.526284
							EA	.0035	2.5263563
2	1	2		1	1	1	AA	-.0094	2.5384458
2	0	2		1	0	1	AA	-.0068	2.598873
2	1	1		1	1	0	AA	-.0076	2.6653508
4	2	3		4	1	3	AA	.0312	2.6774551
6	2	5		5	3	3	AA	-.0001	2.7845499
							EA	.0069	2.7848117
							EE^+	.0091	2.7849103
							EE-	.0108	2.7847315
3	0	3		2	1	1	AA	-.0224	2.7963023
3	2	2		3	1	2	AA	.0068	2.8003598
2	2	1		2	1	1	AA	-.0028	2.8935934
							EA	-.0061	2.8934752
6	2	4		5	3	2	AA	-.0041	2.9846165
							EA	.0127	2.9841564
							EE+	-.0016	2.9840505
							EE-	.0002	2.9842328
5	1	5		4	2	3	AA	.0201	3.0224945
2	2	0		2	1	2	AA	.0045	3.0869848
							EA	-.0027	3.0871211
3	2	1		3	1	3	AA	.0072	3.1960748
4	2	2		4	1	4	AA	-.0147	3.3562557
8	3	5		7	4	3	AA	-.0131	3.5166831
							AE	-.0142	3.5166012
5	2	3		5	1	5	AA	.0091	3.5790609
							EA	-.0036	3.5789745
2	1	1		1	0	1	AA	.0195	3.6933625
							EA	-.0071	3.6933126
3	1	3		2	1	2	AA	.0092	3.8058375
							EA	-.0061	3.8058
6	2	4		6	1	6	AA	.0198	3.8766493
							EA	.0008	3.8764971
11	3	9		11	2	9	AA	.0951	3.8875012

3	0	3	2	0	2	AA	-.0186	3.8907693
3	2	2	2	2	1	AA	.0081	3.9028551
						EE+	-.0143	3.9029396
3	2	1	2	2	0	AA	-.0005	3.9149152
						EA	-.0058	3.914761
5	1	4	4	2	2	AA	-.0001	3.9267244
						EA	.0084	3.926606
4	0	4	3	1	2	AA	-.0342	3.9741203
3	1	2	2	1	1	AA	-.0227	3.9960675
7	2	6	6	3	4	AA	-.0122	4.0477758
						EA	.0001	4.047825
6	1	6	5	2	4	AA	.0001	4.1179884
10	3	8	10	2	8	AA	.0929	4.1556482
7	2	5	7	1	7	AA	.0494	4.2601906
9	3	7	9	2	7	AA	.0788	4.3868742
7	2	5	6	3	3	AA	-.0051	4.3933869
						EA	.0107	4.393108
8	3	6	8	2	6	AA	.0349	4.5772823
						EA	.0115	4.5773451
7	3	5	7	2	5	AA	.0405	4.7254123
						EA	-.0463	4.7253537
9	3	7	8	4	5	AA	-.0074	4.788042
						EA	.0096	4.788776
						EE-	.0074	4.7886016
6	3	4	6	2	4	AA	-.0036	4.8326854
						EA	-.0167	4.832601
5	3	3	5	2	3	AA	-.0032	4.9039287
						EA	-.0027	4.903624
						EE+	.0007	4.903528
						EE-	-.0045	4.903707
5	3	2	5	2	3	EA	-.0067	4.906833
						EE+	-.0053	4.906925
						EE-	-.0021	4.906749
4	3	2	4	2	2	AA	-.0074	4.9462942
						EA	.0062	4.945604
						EE+	.0114	4.945462
						EE-	.0033	4.94574
3	3	1	3	2	1	AA	.0049	4.9680465
						EA	.0047	4.9670947
						AE	.0126	4.9679419
						EE+	.0028	4.9669336
						EE-	-.0024	4.9672398
3	3	1	3	2	2	AA	-.0989	4.98304
						EA	.0061	4.982248
						EE+	.0058	4.982107
						EE-	.0057	4.982384
3	3	0	3	2	2	AA	.0054	4.9832348

						EA	-.0045	4.9842331
						AE	.0016	4.9833377
						EE+	-.0011	4.9843901
						EE-	-.0035	4.9840763
4	3	1	4	2	3	AA	.0056	4.9919125
						EA	-.0020	4.9926676
						AE	.0149	4.9919518
						EE+	-.0032	4.9928079
						EE-	.0010	4.992526
5	3	3	5	2	4	EA	.0003	5.007153
						EE+	.0007	5.007057
						EE-	-.0006	5.007235
5	3	2	5	2	4	AA	.0148	5.010012
						EA	.0020	5.0103677
						EE+	.0003	5.0104596
						EE-	.0045	5.0102797
6	3	3	6	2	5	AA	.0060	5.0428268
						EA	-.0085	5.0429533
4	1	4	3	1	3	AA	.0188	5.0711194
						EA	-.0102	5.0710624
3	1	2	2	0	2	AA	-.0223	5.0905311
5	0	5	4	1	3	AA	-.0259	5.0959138
7	3	4	7	2	6	AA	.0134	5.0972387
4	0	4	3	0	3	AA	-.0305	5.1738894
7	1	7	6	2	5	AA	.0393	5.1761109
8	3	5	8	2	7	AA	.0034	5.1817688
4	2	3	3	2	2	AA	.0174	5.2014453
						EA	-.0153	5.2013849
4	3	2	3	3	1	AA	-.0026	5.2095608
						EA	.0036	5.2097413
						AE	-.0017	5.2096375
4	3	1	3	3	0	AA	.0012	5.2101066
						EA	.0030	5.2098352
						AE	-.0072	5.2100215
4	2	2	3	2	1	AA	.0026	5.231306
						EA	.0021	5.231232
9	3	6	9	2	8	AA	-.0052	5.3067836
						EA	-.0130	5.3067248
4	1	3	3	1	2	AA	.0033	5.3243603
						EA	.0070	5.324302
6	1	5	5	2	3	AA	.0050	5.3393371
						EA	.0096	5.339198
10	3	7	10	2	9	AA	-.0756	5.4842286
2	2	0	1	1	0	AA	.0046	5.5619879
						EA	.0015	5.562117
2	2	1	1	1	1	AA	.0002	5.622407
						EA	-.0078	5.62225

8	2	6	7	3	4	AA	.0089	5.8372574
						EA	.0140	5.8370058
6	0	6	5	1	4	AA	.0071	6.1533411
						EA	-.0431	6.1532755
10	3	7	9	4	5	AA	-.0256	6.2404487
						EE-	-.0136	6.239861
5	1	5	4	1	4	AA	.0088	6.3337809
						EA	-.0157	6.3337244
5	0	5	4	0	4	AA	-.0315	6.4461107
5	2	4	4	2	3	AA	-.0266	6.4979579
5	3	3	4	3	2	AA	-.0147	6.514169
						EA	.0087	6.514514
						AE	.0237	6.514231
5	3	2	4	3	1	AA	.0114	6.5160862
						EA	-.0021	6.515626
						AE	.0359	6.5160862
4	1	3	3	0	3	AA	-.0252	6.5240973
5	2	3	4	2	2	AA	-.0110	6.5565424
						EA	-.0014	6.556475
5	1	4	4	1	3	AA	.0045	6.6491257
						EA	.0038	6.6490467
7	1	6	6	2	4	AA	.0041	6.7312976
						EA	.0059	6.7311413
10	4	7	10	3	7	AA	-.0369	6.8028038
						EA	.0104	6.8026794
						EE+	.0400	6.8026254
3	2	1	2	1	1	AA	.0132	6.8115537
9	4	6	9	3	6	AA	-.0104	6.868284
						EA	.0115	6.8678436
						EE+	.0204	6.8677064
						EE-	.0220	6.8679803
8	4	5	8	3	5	AA	-.0246	6.9112187
7	4	4	7	3	4	AA	.0106	6.9381709
						EA	-.0045	6.9369965
						AE	.0026	6.9380728
						EE+	-.0029	6.9367831
						EE-	-.0127	6.9371923
7	4	3	7	3	4	EA	-.0067	6.939672
						EE+	-.0024	6.93985
						EE-	-.0030	6.939492
9	4	5	9	3	7	AA	.0070	6.951348
						EA	-.0153	6.951895
						EE+	-.0210	6.952027
						EE-	-.0118	6.951764
8	4	5	8	3	6	EA	-.0058	6.951147
						EE+	-.0108	6.950963
6	4	3	6	3	3	EA	.0024	6.952839

						AE	.0084	6.9540495
						EE+	.0074	6.952604
						EE-	.0046	6.953068
6	4	2	6	3	3	EA	-.0146	6.955479
						AE	.0088	6.954455
						EE+	-.0017	6.955644
						EE-	-.0104	6.955318
10	4	6	10	3	8	AA	.0112	6.9551669
7	4	3	7	3	5	AA	.0133	6.9572535
						EA	.0046	6.9584927
						AE	.0147	6.9573369
						EE+	.0075	6.9587026
						EE-	.0175	6.9582936
6	4	2	6	3	4	AA	.0024	6.9618409
						AE	.0024	6.961992
5	4	2	5	3	2	AA	.0030	6.963208
						EA	.0136	6.9615958
						AE	.0006	6.9630066
5	4	1	5	3	2	EA	-.0025	6.9642368
						EE+	-.0046	6.964332
						EE-	-.0018	6.9641239
5	4	2	5	3	3	EA	-.0022	6.964793
						EE+	-.0009	6.964689
						EE-	-.0068	6.964894
5	4	1	5	3	3	AA	.0142	6.9657629
						AE	-.0003	6.9659395
4	4	1	4	3	1	AA	.0490	6.9679354
						AE	.0233	6.9676779
						EE+	.0249	6.9655525
4	4	0	4	3	2	AA	-.0006	6.9685205
3	2	2	2	1	2	AA	-.0178	6.9867808
						EA	-.0137	6.986725
7	0	7	6	1	5	AA	-.0474	7.1398643
6	1	6	5	1	5	AA	-.0260	7.5934724
6	0	6	5	0	5	AA	.0096	7.7065252
						EA	.0110	7.7064684
6	2	5	5	2	4	AA	-.0102	7.7920134
						EA	.0075	7.791965
6	3	4	5	3	3	AA	-.0162	7.819817
						EA	-.0135	7.819961
6	3	3	5	3	2	AA	-.0108	7.8248364
						EA	-.0016	7.824552
6	2	4	5	2	3	AA	-.0123	7.8910638
						EA	-.0055	7.890978
6	1	5	5	1	4	AA	-.0010	7.96916
						EA	.0003	7.9690675
5	1	4	4	0	4	AA	-.0091	7.9993146

						EA	.0108	7.9992387
8	1	7	7	2	5	AA	.0126	8.086786
						EA	.0039	8.086613
4	2	3	3	1	3	AA	-.0393	8.382359
7	1	7	6	1	6	AA	-.0329	8.850074
3	3	0	2	2	0	AA	.0052	8.883053
						EA	.0095	8.883862
						AE	.0387	8.883189
						EE+	.0323	8.883987
						EE-	.0018	8.883741
3	3	1	2	2	1	AA	.0271	8.886013
						EA	.0115	8.885175
						AE	.0059	8.885883
						EE+	-.0021	8.885053
						EE-	.0405	8.885311
10	5	6	10	4	6	AA	-.0125	8.920641
						AE	-.0044	8.920457
10	5	5	10	4	7	AA	-.0112	8.927387
						AE	-.0068	8.927573
9	5	5	9	4	5	AA	.0057	8.935516
						AE	.0014	8.935272
9	5	4	9	4	6	AA	.0003	8.938407
						AE	-.0110	8.938625
8	5	4	8	4	4	AA	.0048	8.945782
						AE	.0067	8.945507
8	5	3	8	4	5	AA	.0051	8.946897
						AE	-.0065	8.947152
7	5	3	7	4	3	AA	-.0002	8.952715
7	5	2	7	4	4	AA	-.0146	8.953072
7	0	7	6	0	6	AA	-.0626	8.955676
7	3	4	6	3	3	AA	-.0113	9.1374644
7	2	5	6	2	4	AA	.0271	9.2336457
						EA	.0122	9.2335194
7	1	6	6	1	5	AA	.0144	9.283052
						EA	-.0064	9.282924
9	1	8	8	2	6	AA	.0072	9.391
						EA	.0007	9.390836
6	1	5	5	0	5	AA	.0075	9.52235
						EA	.0189	9.522225
4	3	1	3	2	1	AA	.0155	10.178253
						EA	-.0089	10.178909
						EE+	-.0086	10.179038
						EE-	-.0214	10.178762
4	3	2	3	2	2	EA	-.0006	10.191979
						EE+	-.0135	10.191831
						EE-	.0133	10.192121
8	4	5	7	4	4	EA	-.0022	10.428475

						AE	-.0069	10.428351
8	4	4	7	4	3	AA	.0131	10.429053
						EA	-.0062	10.428661
						AE	-.0381	10.42895
8	3	5	7	3	4	AA	.0034	10.455228
						EA	-.0019	10.455085
6	2	4	5	1	4	EA	-.0043	10.520858
8	2	6	7	2	5	AA	-.0082	10.581324
						EA	.0307	10.581232
8	1	7	7	1	6	AA	-.0085	10.58909
						EA	-.0060	10.588975
9	6	3	9	5	5	AA	-.0147	10.941064
6	2	5	5	1	5	AA	-.0008	11.267533
						EA	-.0316	11.267378
5	3	2	4	2	2	AA	.0001	11.463009
						EA	-.0041	11.463312
5	3	3	4	2	3	AA	-.0011	11.505457
						EA	.0293	11.505114
9	6	3	8	6	2	AA	-.0013	11.723122
						EA	-.0097	11.723
9	6	4	8	6	3	AA	-.0009	11.723122
						EA	-.0123	11.723
9	5	4	8	5	3	AA	-.0087	11.72805
						EA	-.0011	11.727925
9	4	6	8	4	5	AA	.0141	11.736558
						EA	-.0105	11.736783
9	4	5	8	4	4	AA	.0090	11.738299
						EA	.0209	11.73783
9	3	7	8	3	6	AA	.0227	11.740044
						EA	.0318	11.739951
9	3	6	8	3	5	AA	.0072	11.7795
						EA	.0012	11.779354
9	1	8	8	1	7	AA	.0104	11.885562
						EA	-.0126	11.885415
4	4	1	3	3	1	AA	-.0263	12.178056
						EA	-.0220	12.177675
7	2	6	6	1	6	AA	.0175	12.757124
						EA	.0071	12.756946
10	7	3	10	6	5	AA	.0098	12.934355
						EA	.0140	12.938745
						EE-	-.0039	12.938083
9	7	2	9	6	4	AA	-.0024	12.938363
						EE+	.0163	12.9434
9	7	3	9	6	3	AA	-.0019	12.938363
						EE-	-.0152	12.93474
10	7	3	9	7	2	AA	.0034	13.024346
						EA	-.0029	13.024214

10	7	4	9	7	3	AA	.0034	13.024346
						EA	-.0057	13.024214
10	6	4	9	6	3	AA	.0048	13.028369
						EA	.0084	13.028245
10	6	5	9	6	4	AA	.0062	13.028369
						EA	.0052	13.028245
10	3	8	9	3	7	AA	.0204	13.046116
						EA	-.0309	13.045944
10	4	6	9	4	5	AA	-.0223	13.049888
						EA	-.0028	13.049511
10	1	9	9	1	8	AA	.0135	13.170673
						EA	.0171	13.17055
5	4	2	4	3	2	AA	-.0173	13.479895
						EA	-.0035	13.479297
						AE	-.0129	13.479741
7	3	5	6	2	5	AA	.0094	14.161594
						EA	-.0082	14.161451
8	2	7	7	1	7	AA	.0349	14.277719
						EA	.0093	14.277471
9	2	7	8	1	7	AA	.0269	14.425059
						EA	.0343	14.42495
11	1	10	10	1	9	AA	-.0221	14.443063
						EA	-.0473	14.442912
6	4	2	5	3	2	AA	.0049	14.779153
						EA	.0268	14.780074
						AE	.0118	14.779299
						EE-	.0017	14.779935
6	4	3	5	3	3	AA	.0050	14.781576
						EA	-.0013	14.780602
						AE	.0022	14.781425
12	1	12	11	1	11	EA	-.0110	15.091044
5	5	0	4	4	0	EA	.0033	15.471801
						AE	-.0198	15.4715
5	5	1	4	4	1	EA	.0169	15.47115
12	4	9	11	4	8	AA	.0114	15.669152
						EA	-.0122	15.669031
12	4	8	11	4	7	AA	.0001	15.682796
						EA	.0032	15.682574
12	3	9	11	3	8	AA	-.0634	15.80215
						EA	-.0526	15.801963
10	2	8	9	1	8	EA	-.0044	15.816652
7	4	3	6	3	3	AA	.0080	16.076012
						EA	-.0145	16.076971
						EE-	-.0218	16.0768
10	1	9	9	0	9	AA	-.1012	16.161712
6	5	2	5	4	2	AA	-.0028	16.773188
						EA	-.0027	16.772823

						AE	-.0226	16.773104
6	5	1	5	4	1	EA	-.0010	16.773489
9	3	7	8	2	7	AA	.0030	16.881061
						EA	-.0336	16.880886
13	3	11	12	3	10	AA	.0048	16.95266
						EA	.0479	16.952547
13	4	10	12	4	9	AA	-.0119	16.982005
						EA	.0043	16.981878
11	2	9	10	1	9	AA	.0059	17.265026
13	2	11	12	2	10	AA	-.1188	17.277099
						EA	-.0453	17.276966
10	2	9	9	1	9	AA	.0291	17.408575
						EA	-.0330	17.408125
11	1	10	10	0	10	AA	.0009	17.942727
							RMS	10.8 kHz

Table S16. Cartesian coordinates of the five lowest energy conformers of linalool in the principal axes of inertia calculated at the MP2/6-311++G(d,p) level of theory.

	Conformer I				Conformer II		
	a/Å	b/Å	c/Å		a/Å	b/Å	c/Å
O	-0.92699700	-0.15497500	1.40155300	O	0.80735900	-0.11480100	1.36279900
C	-1.65040700	-0.19164400	0.17147700	C	1.54047700	0.38133300	0.24090700
C	-1.11807900	-1.30794500	-0.74744300	C	0.63687400	1.24205500	-0.66237300
C	0.29270000	-1.07110300	-1.31537500	C	-0.37235600	0.46035000	-1.52714400
C	-3.09489100	-0.49584800	0.56716800	C	2.64693400	1.24792500	0.84128200
C	-1.59954300	1.13416800	-0.55277100	C	2.16012500	-0.73616800	-0.56635900
C	1.36086000	-1.06604400	-0.25592300	C	-1.25660500	-0.49664200	-0.76160700
C	2.24837300	-0.08679300	0.03167000	C	-2.32314500	-0.15640900	-0.00344100
C	3.25986500	-0.27112200	1.13540100	C	-3.12220800	-1.19953900	0.73381800
C	2.34497300	1.22923000	-0.69448900	C	-2.78318100	1.26459900	0.19053800
C	-1.05655700	2.25813100	-0.06091800	C	2.10057600	-2.03805900	-0.24798700
H	-1.13363700	-2.24324500	-0.17254900	H	0.10711400	1.94476500	-0.00675000
H	-1.81942800	-1.42599700	-1.58419200	H	1.27628200	1.83618400	-1.32911000
H	0.30371700	-0.14224800	-1.89314300	H	0.17844400	-0.10962700	-2.28291400
H	0.50999000	-1.88529500	-2.02060700	H	-0.98737600	1.18764000	-2.07153100
H	-3.14847600	-1.48525200	1.03224700	H	2.20384000	2.10826900	1.35295800
H	-3.43892500	0.25373200	1.28536900	H	3.21402000	0.65778700	1.56674500
H	-3.75039500	-0.47542700	-0.30911700	H	3.32853400	1.60468400	0.06271900
H	-2.06781300	1.14739000	-1.53893800	H	2.70165500	-0.42210400	-1.46085300
H	1.41799400	-1.97876900	0.34282500	H	-1.00324500	-1.55563700	-0.82980000
H	0.01203000	-0.13010400	1.16965800	H	-0.04621100	-0.41788700	1.02434700
H	3.15855500	-1.24729900	1.61734100	H	-3.12319600	-0.99436000	1.81151700
H	3.14480400	0.50773300	1.89934400	H	-2.72007700	-2.20334500	0.57112100
H	4.27888200	-0.18225500	0.73972500	H	-4.16813500	-1.18661100	0.40427200
H	1.56078700	1.36808900	-1.43890300	H	-2.59511900	1.58793800	1.22214200
H	2.28471400	2.05946000	0.01965000	H	-2.28195400	1.96429600	-0.48142400
H	3.31937900	1.30628700	-1.19301700	H	-3.86418500	1.33725500	0.02294700
H	-1.07347700	3.18259200	-0.63017700	H	2.58163600	-2.78774800	-0.86872100
H	-0.60213500	2.27003500	0.92488600	H	1.58273200	-2.36571400	0.64792600

	Conformer III				Conformer IV		
	a/Å	b/Å	c/Å		a/Å	b/Å	c/Å
O	-0.92699700	-0.15497500	1.40155300	O	-1.70386100	0.86080900	-1.13671500
C	-1.65040700	-0.19164400	0.17147700	C	-1.82100200	0.43229500	0.22380000
C	-1.11807900	-1.30794500	-0.74744300	C	-0.38040100	0.25325500	0.72000300
C	0.29270000	-1.07110300	-1.31537500	C	0.43683200	-0.76631500	-0.08536900
C	-3.09489100	-0.49584800	0.56716800	C	-2.52606800	1.51569600	1.04488100
C	-1.59954300	1.13416800	-0.55277100	C	-2.58902200	-0.86251500	0.34147800
C	1.36086000	-1.06604400	-0.25592300	C	1.85542500	-0.83765800	0.41222700
C	2.24837300	-0.08679300	0.03167000	C	2.89195900	-0.09673100	-0.03293600
C	3.25986500	-0.27112200	1.13540100	C	4.26683500	-0.23727200	0.56860800
C	2.34497300	1.22923000	-0.69448900	C	2.78184300	0.92027900	-1.13983800
C	-1.05655700	2.25813100	-0.06091800	C	-3.01906000	-1.60309300	-0.69158700
H	-1.13363700	-2.24324500	-0.17254900	H	0.11328100	1.23236200	0.66732200
H	-1.81942800	-1.42599700	-1.58419200	H	-0.40619100	-0.04191300	1.77746600
H	0.30371700	-0.14224800	-1.89314300	H	0.39951800	-0.49247700	-1.14294100
H	0.50999000	-1.88529500	-2.02060700	H	-0.02977900	-1.75403500	0.00102700
H	-3.14847600	-1.48525200	1.03224700	H	-1.97153700	2.45553600	0.96455500
H	-3.43892500	0.25373200	1.28536900	H	-3.54625400	1.67282600	0.67472800
H	-3.75039500	-0.47542700	-0.30911700	H	-2.58902600	1.22689700	2.09908100
H	-2.06781300	1.14739000	-1.53893800	H	-2.79753400	-1.18852800	1.36166300
H	1.41799400	-1.97876900	0.34282500	H	2.04697700	-1.52778800	1.23605400
H	0.01203000	-0.13010400	1.16965800	H	-2.59276000	1.07841600	-1.43995000
H	3.15855500	-1.24729900	1.61734100	H	4.60381700	0.71676000	0.99243000
H	3.14480400	0.50773300	1.89934400	H	4.99698000	-0.52236300	-0.19891100
H	4.27888200	-0.18225500	0.73972500	H	4.28368500	-0.99277000	1.35903500
H	1.56078700	1.36808900	-1.43890300	H	3.11537200	1.90159800	-0.78025800
H	2.28471400	2.05946000	0.01965000	H	3.43929000	0.64754200	-1.97488700
H	3.31937900	1.30628700	-1.19301700	H	1.76467700	1.02713900	-1.52168300
H	-1.07347700	3.18259200	-0.63017700	H	-3.57538200	-2.52035600	-0.52639500
H	-0.60213500	2.27003500	0.92488600	H	-2.80495200	-1.31523400	-1.71619900

	Conformer V		
	a/Å	b/Å	c/Å
O	-2.32992800	-0.82653500	1.04613700
C	-1.88907500	-0.38146400	-0.23944100
C	-0.40311000	-0.75471500	-0.32058500
C	0.45718300	-0.14962700	0.79698100
C	-2.67276300	-1.11117500	-1.33414600
C	-2.06455500	1.10931700	-0.41003300
C	1.88977800	-0.59212500	0.67176500
C	2.87152600	0.05467100	0.00887700
C	4.26520900	-0.51402100	-0.07094900
C	2.68123600	1.36959700	-0.70288300
C	-2.45855100	1.95671000	0.55307900
H	-0.32943600	-1.84969300	-0.28801100
H	-0.01328200	-0.43135500	-1.29498200
H	0.05379700	-0.47008500	1.76277700
H	0.37815700	0.94124200	0.76863500
H	-2.55286400	-2.19182600	-1.21191100
H	-3.73903200	-0.86284700	-1.27138900
H	-2.31548200	-0.82230500	-2.32798300
H	-1.84992400	1.49161400	-1.40931100
H	2.14034600	-1.55008000	1.13097500
H	-3.28436000	-0.69396600	1.07675600
H	4.55656000	-0.68150300	-1.11522300
H	4.34194600	-1.46323800	0.46639600
H	4.99367500	0.18600400	0.35660400
H	2.94770800	1.26503200	-1.76201500
H	1.65595300	1.74070000	-0.64527800
H	3.34774900	2.13208000	-0.28089100
H	-2.56964500	3.01741300	0.35107300
H	-2.65736300	1.60647400	1.56124600