A scent of peppermint – a microwave spectroscopy analysis on the composition of peppermint oil

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Table S1: Experimentally determined rotational constants for the parent and the ^{13}C singly substituted isotopologues of the lowest energy conformer of menthol EQ1ext

	parent	^{13}C1	^{13}C2	^{13}C3
A / MHz	1779.79549(38)	1778.520(21)	1766.036(32)	1767.551(35)
B / MHz	692.62171(24)	687.83895(38)	690.62144(55)	692.60182(65)
C / MHz	573.34542(27)	570.10533(38)	570.57274(57)	572.10424(65)
Δ_J / kHz	0.0166(31)	$[0.0166]^a$	[0.0166	[0.0166]
N_{lines}^a	53	18	15	18
σ / kHz	5.5	4.5	6.2	7.6

	^{13}C4	^{13}C5	^{13}C6	^{13}C7
A / MHz	1778.999(32)	1772.165(20)	1773.397(40)	1779.066(19)
B / MHz	692.09869(58)	692.60432(35)	690.24117(64)	679.85356(31)
C / MHz	573.07264(55)	572.57490(34)	571.08109(62)	564.49456(30)
Δ_J / kHz	[0.0166	[0.0166]	[0.0166]	[0.0166]
N_{lines}^a	16	16	14	16
σ / kHz	6.0	4.0	6.8	3.4

	^{13}C8	^{13}C9	^{13}C10
A / MHz	1779.760(15)	1768.555(27)	1767.8522(51)
B / MHz	688.10319(25)	684.62415(41)	683.66536(33)
C / MHz	570.25610(26)	569.01801(42)	566.99232(28)
Δ_J / kHz	[0.0166]	[0.0166]	[0.0166]
N_{lines}^b	17	17	21
σ / kHz	3.0	4.9	4.8

[a] fixed to the value determined for the parent species.
[b] number of rotational transitions in the fit.

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Table S2: r_s structure, x, y and z coordinates of the isotopically substituted atoms of menthol EQ1ext, and their comparison with r_0, r_e (B3LYP/def2-TZVPP) structures. All coordinates are in Å.

	atom	x	y	z
r_s		2.22553(78)	−0.2660(65)	0.3680(47)
r_0	C1	2.2291(18)	−0.267(14)	0.3795(85)
r_e		2.228	−0.227	0.383
r_s		1.4451(14)	−1.4859(14)	−0.147(14)
r_0	C2	1.4511(29)	−1.4878(31)	−0.1517(63)
r_e		1.446	−1.471	−0.044
r_s		−0.130i(16)	−1.3909(15)	0.196(11)
r_0	C3	−0.045(19)	−1.3951(27)	0.1913(87)
r_e		−0.043	−1.346	0.276
r_s		−0.6505(31)	−0.048i(41)	−0.3605(55)
r_0	C4	−0.6663(45)	−0.097(12)	−0.3627(30)
r_e		−0.671	−0.101	−0.367
r_s		0.095i(18)	1.0948(16)	0.166(10)
r_0	C5	0.1070(63)	1.0991(27)	0.1973(60)
r_e		0.103	1.140	0.079
r_s		1.5820(14)	1.0050(22)	−0.153(15)
r_0	C6	1.5820(26)	1.0098(47)	−0.203(18)
r_e		1.591	1.016	−0.241
r_s		3.70705(46)	−0.3474(49)	0.017i(98)
r_0	C7	3.7091(11)	−0.3633(90)	0.0100(85)
r_e		3.709	−0.335	0.030
r_s		−2.18977(74)	0.073i(22)	−0.105(15)
r_0	C8	−2.1927(17)	0.0281(99)	−0.1396(80)
r_e		−2.194	0.029	−0.143
r_s		−2.59065(72)	0.088i(21)	1.3558(14)
r_0	C9	−2.5932(17)	0.059(23)	1.3582(27)
r_e		−2.598	0.102	1.332
r_s		−2.95832(52)	−1.0665(14)	−0.9058(17)
r_0	C10	−2.9629(16)	−1.0651(46)	−0.9036(37)
r_e		−2.962	−1.087	−0.856

Table S3: Structural parameters obtained from r_0 and r_s fits in comparison to the compu-tationally determined values r_e structure, (B3LYP-D3/def2-TZVPP) for menthol conformer EQ1ext.

	r_s	r_0	r_e
r(C1-C2) / Å	1.5370(72)	1.544(15)	1.53
r(C2-C3) / Å	1.4882(42)	1.525(20)	1.53
r(C3-C4) / Å	1.6332(45)	1.548(14)	1.54
r(C4-C5) / Å	1.3782(49)	1.526(14)	1.53
r(C5-C6) / Å	1.6141(38)	1.5305(86)	1.53
r(C1-C6) / Å	1.5178(79)	[1.53]	1.53
r(C1-C7) / Å	1.5287(15)	1.5332(44)	1.53
r(C4-C8)/ Å	1.5603(41)	1.5497(53)	1.55
r(C8-C9)/ Å	1.515 (15)	1.5487(84)	1.53
r(C8-C10)/ Å	1.5393(82)	1.5415(60)	1.53
∡(C1-C2-C3) / °	111.42(49)	111.46(40)	111.90
∡(C2-C3-C4) / °	111.26(43)	111.56(48)	112.16
∡(C3-C4-C5) / °	110.99(40)	[109.20]	109.20
∡(C4-C5-C6) / °	110.01(44)	110.39(54)	111.47
∡(C5-C6-C1) / °	113.28(49)	[112.69]	112.69
∡(C6-C1-C2) / °	109.49(41)	[109.49]	109.49
∡(C7-C1-C2) / °	111.67(43)	111(1)	111.95
∡(C7-C1-C6) / °	111.99(43)	[111.53]	111.53
∡(C5-C4-C8) / °	113.77(38)	[112.86]	112.86
∡(C3-C4-C8) / °	109.71(31)	[114.25]	114.25
∡(C4-C8-C10) / °	114.04(62)	[111.45]	111.45
∡(C4-C8-C9) / °	114.77(74)	113.19(38)	113.82
∡(C9-C8-C10) / °	111.69(38)	[110.55]	110.55
∡(C7-C1-C2-C3) / °	-179.12(66)	[-178.47]	-178.47
∡(C7-C1-C6-C5) / °	177.65(65)	[179.22]	179.22
∡(C1-C2-C3-C4) / °	55(1)	[56.52]	56.52
∡(C1-C6-C5-C4) / °	-57(1)	[-56.77]	-56.77
∡(C2-C3-C4-C8) / °	174.51(85)	[176.61]	176.61
∡(C3-C4-C8-C9) / °	64.76(47)	57.87(82)	59.55
∡(C3-C4-C8-C10) / °	-65.89(97)	-64.71(79)	-66.30
∡(C5-C4-C3-C2) / °	-58.91(93)	[-55.94]	-55.94
∡(C6-C5-C4-C3) / °	55.86(88)	58.26(99)	55.59
∡(C5-C4-C8-C9) / °	-60.23(54)	[-65.99]	-65.99
∡(C5-C4-C8-C10) / °	169.12(65)	[168.15]	168.15

The distances and angles, which involve C3, C4, C5, C7, C8, and C9 atoms. have been calculated by setting the imaginary r_s coordinates to zero.

Table S4: Experimentally determined rotational constants for the isotopic species of menthone B.

	parent	^{13}C2	^{13}C3	^{13}C4
A / MHz	2021.98637(366)	2013.2668(88)	2021.1247(17)	2005.1551(48)
B / MHz	693.53686(16)	693.54403(89)	693.04103(49)	693.40011(47)
C / MHz	562.13636(16)	561.47905(71)	561.82736(39)	560.92983(35)
Δ_J / kHz	0.0109(18)	[0.0109]^a	[0.0109]	[0.0109]
Δ_{JK} / kHz	0.0473(50)	[0.0473]	[0.0473]	[0.0473]
N^b_{lines}	112	7	12	13
σ / kHz	6.0	6.4	7.6	5.5

	^{13}C5	^{13}C6	^{13}C7	^{13}C8
A / MHz	2005.7371(45)	2021.5275(45)	2011.79560(82)	2021.6409(34)
B / MHz	691.27977(43)	688.59370(41)	691.24026(28)	689.05149(40)
C / MHz	559.39771(30)	558.90281(30)	560.04132(20)	559.19980(25)
Δ_J / kHz	[0.0109]	[0.0109]	[0.0109]	[0.0109]
Δ_{JK} / kHz	[0.0473]	[0.0473]	[0.0473]	[0.0473]
N^b_{lines}	10	11	12	12
σ / kHz	4.1	4.1	3.6	3.7

	^{13}C10	^{13}C11	^{13}C12
A / MHz	2012.1098(48)	2004.821(19)	2021.178(11)
B / MHz	685.08386(44)	685.6815(11)	680.5527(14)
C / MHz	556.38999(35)	555.5508(13)	553.60823(87)
Δ_J / kHz	[0.0109]	[0.0109]	[0.0109]
Δ_{JK} / kHz	[0.0473]	[0.0473]	[0.0473]
N^b_{lines}	14	6	11
σ / kHz	5.6	8.1	11.8

^{a} fixed to the value determined for the parent species.
^{b} number of rotational transitions in the fit.

Table S5: r_s structure, x, y and z coordinates of the isotopically substituted atoms of menthone B, and their comparison with r_0, r_e (B3LYP/def2-TZVPP) structures. All coordinates are in Å.

	atom	x	y	z
r_s		$0.137i(11)$	$1.0366(15)$	$-0.107(15)$
r_0	C2	$0.049(10)$	$1.0432(53)$	$-0.0732(55)$
r_e		0.081	1.093	-0.115
r_s		$-0.6752(23)$	$-0.1999(76)$	$0.2588(59)$
r_0	C3	$-0.7094(99)$	$-0.204(24)$	$0.2532(61)$
r_e		-0.705	-0.169	0.231
r_s		$0.101i(15)$	$-1.3958(11)$	$-0.3953(39)$
r_0	C4	$0.102(21)$	$-1.3927(80)$	$-0.425(19)$
r_e		0.076	-1.358	-0.377
r_s		$1.54116(98)$	$-1.4282(11)$	$0.037(41)$
r_0	C5	$1.5431(70)$	$-1.4370(76)$	$0.050(14)$
r_e		1.532	-1.395	0.084
r_s		$2.28111(67)$	$-0.117(13)$	$-0.2090(73)$
r_0	C6	$2.2862(45)$	$-0.0951(92)$	$-0.206(12)$
r_e		2.285	-0.102	-0.230
r_s		$1.5034(10)$	$1.0544(14)$	$0.4051(37)$
r_0	C7	$1.5007(72)$	$1.066(10)$	$0.441(19)$
r_e		1.519	1.099	0.358
r_s		$-2.17376(70)$	$-0.0.102(15)$	$-0.1812(84)$
r_0	C8	$-2.1802(48)$	$-0.130(36)$	$-0.142(16)$
r_e		-2.182	-0.082	-0.181
r_s		$-2.92087(9)$	$0.8799(17)$	$0.6900(22)$
r_0	C10	$-2.9219(40)$	$0.886(14)$	$0.708(13)$
r_e		-2.920	0.953	0.675
r_s		$-2.90183(60)$	$-1.5072(12)$	$-0.295i(60)$
r_0	C11	$-2.8995(40)$	$-1.5025(79)$	$-0.054(16)$
r_e		-2.902	-1.430	-0.097
r_s		$3.72379(44)$	$-0.155(11)$	$0.2804(58)$
r_0	C12	$3.72624(29)$	$-0.1363(99)$	$0.303(19)$
r_e		3.726	-0.136	0.269

Table S6: Structural parameters obtained from r_0 and r_s fits in comparison to the computa-tionally determined values (r_e structure, B3LYP-D3/def2-TZVPP) for menthone B.

	r_0	r_s	r_e
r(C2-C3) / Å	1.4555(78)	1.496(25)	1.53
r(C3-C4) / Å	1.5211(68)	1.591(26)	1.55
r(C4-C5) / Å	1.601(11)	1.518(21)	1.53
r(C5-C6) / Å	1.5255(13)	1.555(13)	1.53
r(C6-C7) / Å	1.534(10)	[1.54]	1.54
r(C2-C7) / Å	1.5882(50)	1.540(12)	1.51
r(C3-C8) / Å	1.5649(38)	1.5247(14)	1.54
r(C8-C10) / Å	1.510(11)	1.519(21)	1.53
r(C8-C11)/ Å	1.5933(12)	1.552(34)	1.53
r(C6-C12)/ Å	1.5239(31)	1.5279(62)	1.53
∡(C2-C3-C4) / °	110.73(41)	105.74(64)	106.64
∡(C2-C3-C8) / °	108.68(69)	113(2)	112.80
∡(C2-C7-C6) / °	110.02(38)	[112.80]	110.48
∡(C3-C2-C7) / °	111.58(51)	[110.48]	114.93
∡(C3-C4-C5) / °	109.09(82)	[114.93]	112.41
∡(C3-C8-C10) / °	110.63(65)	111(1)	110.58
∡(C3-C8-C11) / °	110.50(81)	113(3)	112.82
∡(C4-C3-C8) / °	110.70(61)	[115.06]	115.06
∡(C4-C5-C6) / °	114(1)	112.13(52)	112.77
∡(C5-C6-C7) / °	110.22(78)	[109.63]	109.63
∡(C5-C6-C12) / °	113(1)	[112.29]	112.29
∡(C7-C6-C12) / °	111.73(70)	[111.23]	111.23
∡(C10-C8-C11) / °	106.36(35)	[109.73]	109.73
∡(C2-C3-C4-C5) / °	57(1)	56.76(99)	54.73
∡(C3-C4-C5-C6) / °	-53(3)	[-56.69]	-56.69
∡(C4-C5-C6-C7) / °	51(3)	[54.25]	54.25
∡(C4-C5-C6-C12) / °	177(2)	[178.42]	178.42
∡(C5-C6-C7-C2) / °	-53(2)	[-53.52]	-53.52
∡(C2-C7-C6-C12) / °	-178.77(67)	[-178.31]	-178.31
∡(C2-C3-C8-C10) / °	-70.86(92)	-67(3)	-68.24
∡(C2-C3-C8-C11) / °	171.62(69)	[168.45]	168.45
∡(C4-C3-C8-C10) / °	167.32(59)	[169.11]	169.11
∡(C4-C3-C8-C11) / °	49.79(64)	[45.80]	45.80
∡(C7-C2-C3-C8) / °	175.81(68)	[175.85]	175.85
∡(C5-C4-C3-C8) / °	178(1)	[-179.38]	-179.38

The distances and angles which involve C2, C4, and C11 atoms have been calculated by setting the imaginary r_s coordinates to zero.

Table S7: Measured rotational transitions (ν_{obs}) of menthol EQ3ext and the residuals ($\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$) for the fit reported in the manuscript (Table 2).

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	ν_{obs}(MHz)	$\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$ (MHz)
2	1	2	$\leftarrow$	1	1	1	2411.2536	0.0016
2	0	2	$\leftarrow$	1	0	1	2499.0660	-0.0002
1	1	0	$\leftarrow$	0	0	0	2634.7531	0.0016
7	2	6	$\leftarrow$	7	1	6	2791.5643	-0.0017
6	2	5	$\leftarrow$	6	1	5	3079.8118	0.0055
5	2	4	$\leftarrow$	5	1	4	3336.3109	-0.0032
4	2	3	$\leftarrow$	4	1	3	3555.8358	0.0057
3	1	3	$\leftarrow$	2	1	2	3613.9429	-0.0013
3	0	3	$\leftarrow$	2	0	2	3736.6601	0.0018
3	2	1	$\leftarrow$	2	2	0	3774.9677	0.0004
3	1	2	$\leftarrow$	2	1	1	3891.6573	-0.0035
2	1	1	$\leftarrow$	1	0	1	3979.3134	-0.0002
4	1	4	$\leftarrow$	3	1	3	4813.3304	0.0000
4	0	4	$\leftarrow$	3	0	3	4960.4090	-0.0003
4	2	3	$\leftarrow$	3	2	2	5004.0012	-0.0023
4	3	2	$\leftarrow$	3	3	1	5016.9198	0.0046
4	3	1	$\leftarrow$	3	3	0	5017.8477	-0.0041
4	2	2	$\leftarrow$	3	2	1	5051.3342	-0.0028
4	1	3	$\leftarrow$	3	1	2	5182.8909	-0.0003
3	1	2	$\leftarrow$	2	0	2	5371.9101	0.0017
7	1	6	$\leftarrow$	6	2	4	5615.4418	0.0053
5	1	5	$\leftarrow$	4	1	4	6008.6579	0.0053
5	0	5	$\leftarrow$	4	0	4	6167.1730	0.0056
5	2	4	$\leftarrow$	4	2	3	6248.9950	0.0026
5	4	1	$\leftarrow$	4	4	0	6270.3961	-0.0030
5	3	3	$\leftarrow$	4	3	2	6274.6271	-0.0023
5	3	2	$\leftarrow$	4	3	1	6277.8926	-0.0028
7	3	5	$\leftarrow$	7	2	5	6281.8869	-0.0134
5	2	3	$\leftarrow$	4	2	2	6341.4689	-0.0012
6	3	4	$\leftarrow$	6	2	4	6448.5530	0.0042
5	1	4	$\leftarrow$	4	1	3	6468.5044	-0.0038
2	2	0	$\leftarrow$	1	1	0	6471.8686	-0.0080
2	2	1	$\leftarrow$	1	1	1	6559.6958	0.0047
5	3	3	$\leftarrow$	5	2	3	6560.2156	0.0065
4	3	2	$\leftarrow$	4	2	2	6627.0433	-0.0063
4	3	1	$\leftarrow$	4	2	3	6699.4451	0.0042
5	3	2	$\leftarrow$	5	2	4	6728.3464	0.0023
6	3	3	$\leftarrow$	6	2	5	6780.8723	-0.0044
4	1	3	$\leftarrow$	3	0	3	6818.1424	0.0009
6	1	6	$\leftarrow$	5	1	5	7199.4210	0.0045
6	0	6	$\leftarrow$	5	0	5	7355.9167	0.0032
6	2	5	$\leftarrow$	5	2	4	7490.0096	0.0066
6	4	3	$\leftarrow$	5	4	2	7527.9067	-0.0072
6	4	2	$\leftarrow$	5	4	1	7528.0545	-0.0107
6	3	4	$\leftarrow$	5	3	3	7533.8818	-0.0031
6	3	3	$\leftarrow$	5	3	2	7542.5314	-0.0042
6	2	4	$\leftarrow$	5	2	3	7645.5469	0.0016
3	2	1	$\leftarrow$	2	1	1	7650.3481	0.0047
6	1	5	$\leftarrow$	5	1	4	7746.5114	0.0005
3	2	2	$\leftarrow$	2	1	2	7904.2593	0.0074
							RMS	4.6 kHz