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Supplementary files

Table S1. Comparison of 13C shifts (ppm) from isocommunic acid with 13C shifts from compounds 4–6 by subtraction. Columns 4–6 show difference in 13C shifts compared to 13C shifts of isocommunic acid.

Heading	Δ ^{13}C	δ ^{13}C–δ ^{13}C		
No.	Isocommunic Acid	4	5	6
1	39.9	1.4	1.3	0.7
2	19.8	0.4	0.6	0.4
3	37.9	0.0	−0.1	0.0
4	44.1	0.0	0.2	−0.1
5	56.1	0.5	0.5	0.2
6	22.1	−1.4	0.4	−1.4
7	38.7	1.8	11.3	1.6
8	147.9	87.6	93.8	88.8
9	56.6	8.7	6.3	3.2
10	40.4	−0.2	1.9	−0.6
11	26.0	0.5	−2.4	4.3
12	30.2	−53.6	−2.5	−3.5
13	147	1.1	0.6	−0.2
14	139	2.4	0.4	0.2
15	113.2	−1.8	−0.5	−0.5
16	115.5	0.0	−0.9	−0.5
17	106.4	56.0	−98.8	55.8
18	28.9	−0.2	−0.1	−0.2
19	183.6	1.3	0.9	0.0
20	12.8	−0.5	0.1	−0.4

Table S2. Comparison of ^{13}C shifts for 7 and 8 to cis (*Z*-) and trans (*E*-) communic acids. Column 1 gives ppm difference of 7 and 8 ^{13}C shifts compared to *E*-communic acid and column 2 compares to *Z*-communic acid.

Heading	Column 1			Column 2		
	δ ^{13}C	δ ^{13}C–δ ^{13}C		δ ^{13}C	δ ^{13}C–δ ^{13}C	
No.	*E*-comm	**7** (E-)	**8** (Z-)	*Z*-comm	**7** (E-)	**8** (Z-)
1	39.5	-0.2	-0.3	39.5	-0.2	-0.3
2	20.1	0.7	0.7	20.1	0.7	0.7
3	38.1	0.2	0.2	38.1	0.2	0.2
4	44.4	0.2	0.2	44.4	0.2	0.2
5	56.5	0.7	0.7	56.5	0.7	0.7
6	26.0	2.6	2.6	26.0	2.6	2.6
7	38.7	2.0	2.0	38.7	2.0	2.0
8	148.1	89.3	89.3	148.1	89.3	89.3
9	56.6	2.3	2.1	56.9	2.6	2.4
10	40.6	-0.4	-0.5	40.6	-0.4	-0.5
11	23.5	2.4	3.3	23.5	2.4	3.3
12	134.1	-1.0	1.3	131.9	-3.2	-0.9
13	133.6	0.9	2.7	131.7	-1.0	0.8
14	141.8	0.0	7.9	133.9	-7.9	0.0
15	110.1	-0.1	-3.3	113.4	3.2	0.0
16	12.0	-11.6	-7.9	12.0	-11.6	-7.9
17	107.9	57.6	57.6	108.0	57.7	57.7
18	29.2	0.0	0.0	29.2	0.0	0.0

19	184.4	1.0	0.9	184.4	1.0	0.9
20	13.0	-0.3	-0.3	13.0	-0.3	-0.3

Table S3. 13C NMR shifts (δ, CDCl3) for 8*R*-spiroexpoxy labdanes taken from the literature compared to 4 and 6 and the aldehyde 5: AR [1]; BR [2]; CR & DR [3]; ER, FR & GR [4]; HR [5]. See Figure S2 for the structures.

Epimer	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**	**8R**
Figure	**AR**	**BR**	**CR**	**DR**	**ER**	**FR**	**GR**	**HR**	**4**	**5**	**6**	**7**	**8**
1	40.6	38.9	40.56	42.23	39.4	39.3	39.3	39.2	38.5	38.6	39.2	39.7	39.8
2	19.8	18.6	19.21	19.27	19.3	18.2	19.2	18.7	19.4	19.2	19.4	19.4	19. 5
3	37.7	41.8	37.99	37.84	37.8	35.3	37.7	41.8	37.9	38.0	37.9	37.9	37.9
4	43.9	33.3	44.01	43.89	44.0	40.2	43.9	33.4	44.1	43.9	44.2	44.2	44.2
5	54.8	54.9	55.22	55.08	55.7	55.7	55.7	54.5	55.6	55.6	55.9	55.8	55.8
6	22.9	24.8	23.15	23.26	23.0	21.8	23.3	21.7	23.5	21.7	23.5	23.4	23.4
7	36.0	36.6	36.07	36.21	39.1	38.9	39.1	39.7	36.9	27.4	37.1	36.7	36.7
8	58.1	59.3	58.24	58.93	59.0	58.9	58.8	58.9	60.3	54.1	59.1	58.8	58.9
9	57.4	53.1	57.45	60.49	53.9	51.6	53.8	55.1	47.9	50.3	53.4	54.3	54.5
10	40.8	40.2	39.47	40.4	41.0	38.6	40.9	40.2	40.6	38.5	41	41	41.1
11	140.3	16.1	123.09	65.15	19.5	19.3	19.3	22.5	25.5	28.4	21.7	21.1	20.2
12	135.8	45.0	138.65	66.06	36.8	36.7	36.7	160.4	83.8	32.7	33.7	135.1	132.8
13	197.0	208.9	71.19	51.99	30.0	30.0	30.2	133.8	145.9	146.4	147.2	132.7	130.9
14	27.9	29.8	76.88	-	39.6	39.7	35.3	36.1	136.6	138.6	138.8	141.8	133.9
15	-	-	14.7	-	60.9	60.8	63.0	197.6	115.0	113.7	113.7	110.2	113.4
16	-	-	25.4	20.3	19.6	19.6	19.5	193.7	115.5	116.4	116	23.6	19.9
17	50.5	50.7	50.33	50.63	50.4	50.6	50.2	50.5	50.4	205.2	50.6	50.3	50.3
18	28.8	21.5	28.77	28.75	29.0	27.0	28.9	33.5	29.1	29.0	29.1	29.2	29.2
19	180.0	33.4	177.52	177.3	183.2	67.9	183.3	21.7	182.3	182.7	183.6	183.5	183.5
20	13.9	14.5	13.59	14.42	12.9	15.2	12.9	14.7	13.3	12.7	13.2	13.3	13.3

Table S4. 13C NMR shifts (δ, CDCl3) for 8*S*-spiroexpoxy labdanes taken from the literature: AS [2]; BS & CS [5]: DS & ES [6]. See Figure S3 for the structures.

Epimer	**8S**	**8S**	**8S**	**8S**	**8S**
Figure	**AS**	**BS**	**CS**	**DS**	**ES**
1	38.8	39.6	39.3	40.7	39.6
2	18.5	18.4	18.6	21.6	19.0
3	42.0	42.0	41.9	43.6	42.3
4	33.4	33.6	33.5	34.9	33.9
5	55.0	52.8	52.4	54.9	53.7
6	20.1	20.0	20.0	20.1	20.5
7	35.9	39.6	35.8	37.5	36.3
8	57.1	57.6	57.5	59.7	57.7
9	52.0	55.2	55.0	56.6	55.4
10	40.0	40.0	39.6	41.3	40.2
11	15.6	22.4	22.8	21.2	20.6
12	45.4	161.2	142.8	133.7	140.1
13	208.1	136.0	124.8	139.2	129.1
14	29.7	36.0	25.4	72.3	70.5
15	-	198.0	65.3	66.5	64.5
16	-	194.0	171.2	64.3	65.4
17	48.7	48.8	49.0	50.7	49.4
18	21.7	33.6	33.5	34.5	33.9
19	33.4	21.6	21.7	22.6	22.1
20	14.4	14.8	14.6	15.7	15.0

Table S5. 1H NMR of vinylic protons at the C17 methylene position in the 8*R* or 8*S* spiroepoxy moiety: AR [1]; BS & CS [4]; DS and ES [6].

Epimer	**8*R***	**8*R***	**8*R***	**8R**	**8R**
Figure	**AR**	**4**	**6**	**7**	**8**
C17	2.56, d (4), 2.74, d (4)	2.60, brd (3.89) 2.82, dd (1.97, 3.89)	2.53, d (4.34) 2.76, dd (1.87, 4.34)	2.56, d (4.3) 2.7, dd (1.8, 4.3)	2.55, d (4.3) 2.7, dd (1.8, 4.3)
Epimer	8S	8S	8S	8S	-
Figure	BS	CS	DS	ES	-
C17	2.27, d (3.5) 2.42, d (3.5)	2.29, d (3.9) 2.43, d (3.9)	2.3, d (3.8) 2.7, d (3.8)	2.2, d (3.8) 2.58, d (3.8)	- -

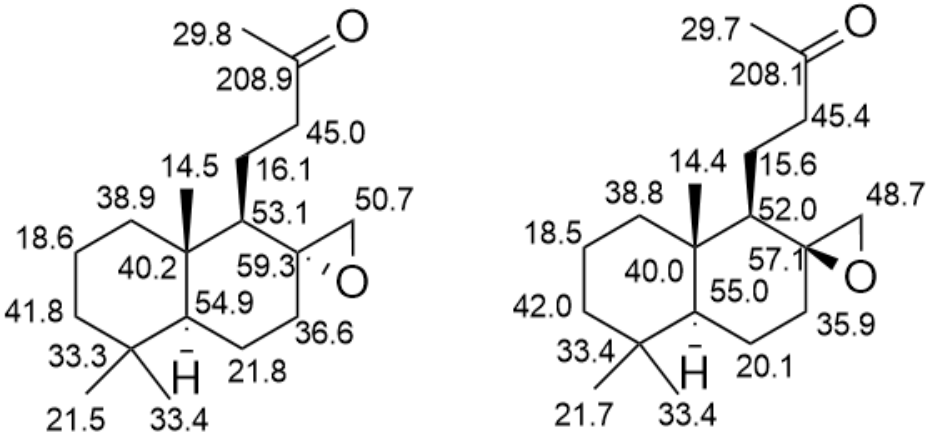

Figure S1. Standard chemical shifts for 8-spiroepoxy labdanes in the *R* and *S* configurations, as proposed by Bastard et al., [2].

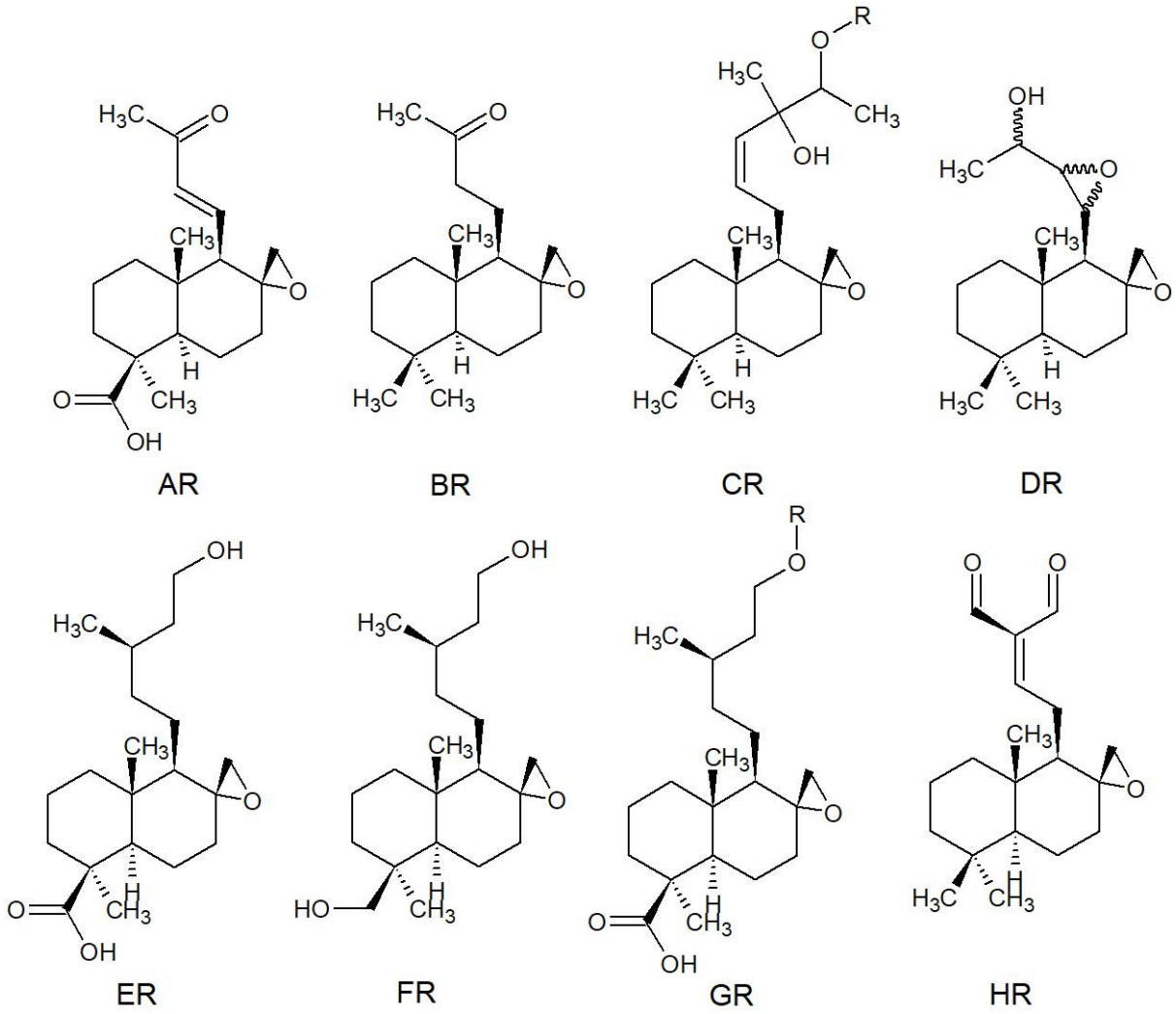

Figure S2. Labdanes with 8*R*-spiroepoxy conformation.

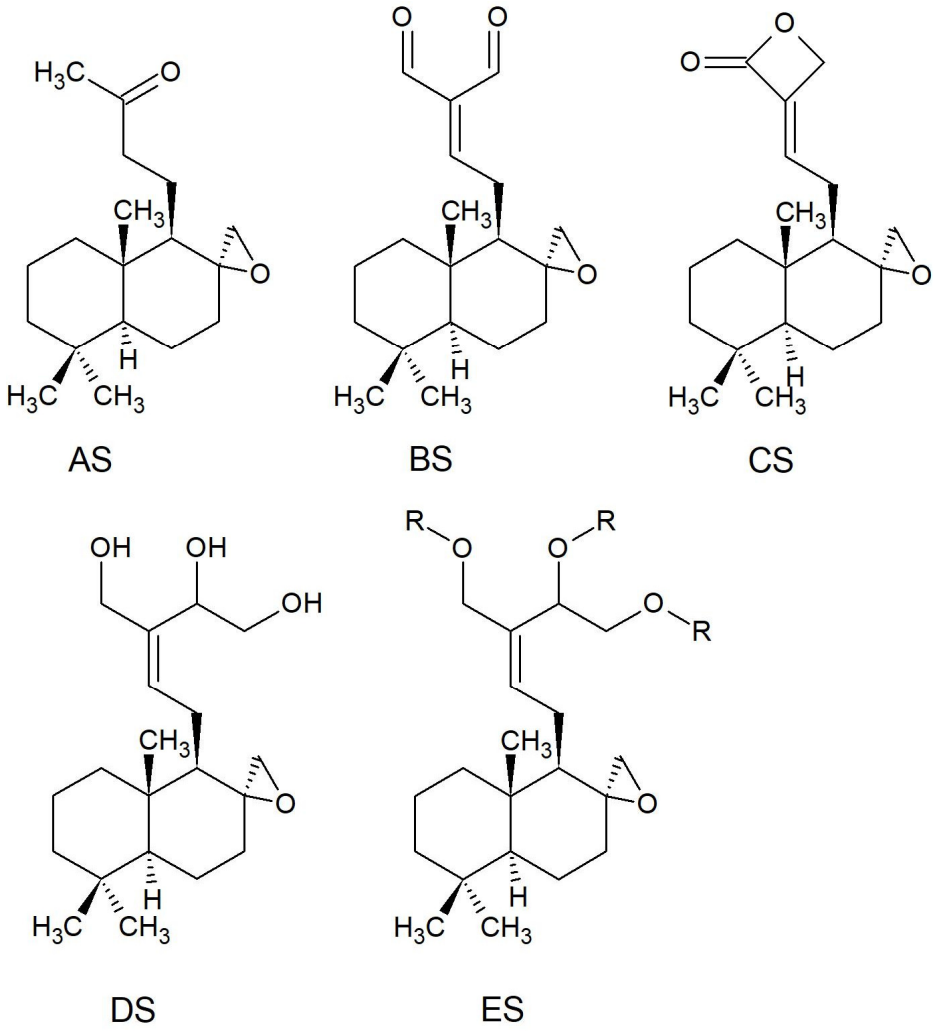

Figure S3. Labdanes with 8*S*-spiroepoxy conformation.

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