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^{13}C NMR Data for Labdane Diterpenoids

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The analysis of the ^{13}C NMR spectra of 91 labdane-type compounds, classified into ten different series, is reported.

KEY WORDS ^{13}C NMR Diterpenes Labdanes Substituted *trans*-decalins 2D NMR

INTRODUCTION

In the course of our research on the isolation and chemical transformations of natural products, a large number of labdane diterpenes and structurally related substances have been obtained.[1–8] In spite of the abundant work in diterpene chemistry, few compilations of ^{13}C NMR data of labdane-type compounds are known.[9] This encouraged us to analyse our ^{13}C NMR spectra in order to provide several sets of data that might serve as models for the assignment of similar compounds in further research.

RESULTS AND DISCUSSION

All the compounds were classified into ten series according to the different substitution of the *trans*-decalin system (Fig. 1). Their structural elucidation was effected by the usual methods (MS, IR, NMR); ^{13}C NMR spectra were obtained by broadband decoupling and DEPT experiments.[10] The assignment of the ^{13}C resonance signals was based on general chemical shift arguments,[11,12] substituent effects[13] and by analogy with decalin models[14,15] and related labdanes.[9,16–19] In order to clarify some questionable assignments the use of H/H and one-bond H/C correlations was desirable and thus we performed 2D NMR experiments on compounds **1A-2**, **1A-31**, **1A-45**, **2A-16**, **4-2**, **6A$_1$-7**, **6B-14**, **7B-54** and **8A-59**, allowing an almost unambiguous assignment for all substances.

Most of the compounds presented here were prepared from the natural products methyl mirceocommunate (**1A-7**), methyl *trans*-communate (**1A-8**), methyl *cis*-communate (**1A-9**) and *cis*-abienol (**6A$_2$-9**) by ozonolysis, oxymercuration–demercuration, hydroboration–oxidation, hydrogenation, epoxidation, photooxidation and other reactions.[1,4–7] Some of the compounds were isolated from *Juniperus oxycedrus* L.[2,3] and *Abies marocana trabut*[8] (for details see Experimental).

Series 1

This series includes dicarbocyclic labdanes with a $\Delta^{8(17)}$ exocyclic double bond. Comparison of the ^{13}C NMR data of the series **1A** compounds (Table 1) reveals the constancy of the chemical shifts for the decalin system, including carbons C-17, -18, -19 and -20. The averaged δ values of these carbons are depicted in Fig. 2, calculated on those compounds with a saturated side-chain (**1A-1**), with Δ^{12}, Δ^{13} and/or Δ^{14} unsaturation (**1A-2** to **1A-9**) and with an oxygenated functionality at C-13, -14, -15 or -16 (**1A-10** to **1A-14**, **1A-16**; **1A-19** to **1A-25**; **1A-27** to **1A-30**). In these compounds only small differences are detected at C-9 depending on whether the double bond is located at Δ^{12} (δ 56.5), Δ^{13} (δ 55.6) or further positions (δ 56.2). However, some of these δ values suffer modifications when the side-chain contains oxygenated groups at C-12 or a Δ^{11} double bond.

In the first case (**1A-31**, **-37**; **1A-41**; **1A-43**) C-9 is the carbon mainly affected by the *γ-gauche* shielding effect of the hydroxyl group (**1A-31** to **1A-33**) or epoxide group (**1A-34** to **1A-37**), or as a consequence of the functional change which occurs in compounds **1A-41** and **1A-43**. Thus, the C-9 shielding is *ca.* 4 ppm for 12-hydroxy derivatives and somewhat lower (*ca.* 2 ppm) for 12,13-epoxy derivatives, according to the more preferred conformation of the side-chain in this type of compound (Fig. 3).[20] The presence of a Δ^{11} double bond (**1A-44**, **-45**, **-46**; **1A-48** to **1A-53**) induces δ variations at the nearest carbons, i.e. C-1, C-9 and C-20, and also C-6, C-7 and the olefinic carbons (C-8, C-17). In spite of the α-effect exerted by the sp^2 C-11 on C-9, this position is only deshielded by *ca.* 4 ppm (averaged δ value of 60.1 ppm). This fact could be explained by the loss of the deshielding H–H *anti* interaction between H-9 and H-11β, existing in labdanes with a saturated C-11—C-12 bond (Fig. 4). In this manner, the loss of the shielding interactions between H-11α and H-1β or H-11β and H-20 (Fig. 4) could also explain the observed deshielding for both carbons (*ca.* 1.5 ppm for C-1; *ca.* 0.8 ppm for C-20).

The replacement of the 4β-carbomethoxy group (series **1A**) by a methyl group (series **1B**) is mainly reflected in the δ changes of C-2, -3, -4, -5, -6, -9, -18 and -20 (Table 2), as stated in the literature.[14] The larger size of the methyl group compared with the flat

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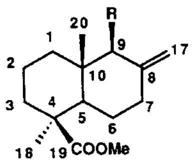
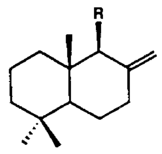
SERIES 1



Series 1A



Series 1B

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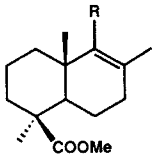

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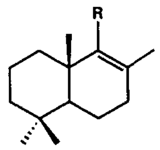

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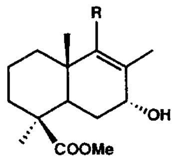

Series 2C

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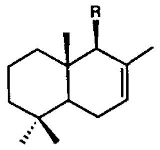

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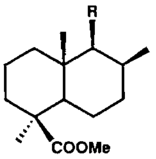
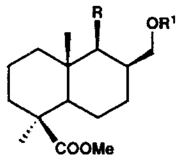
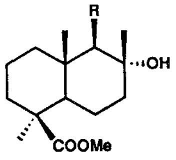


SERIES 5



R^1=Ac: 5-26, -38, -39, -40
R^1=H: 5-7, -9

SERIES 6



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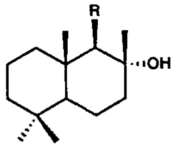

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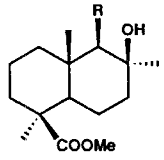
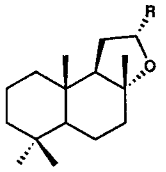


Series 6B

SERIES 7



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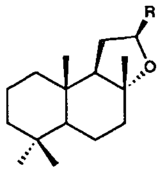

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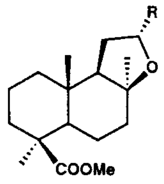
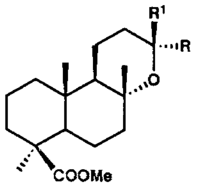


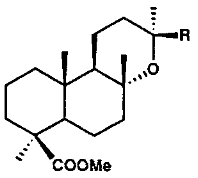
Series 7B

SERIES 8



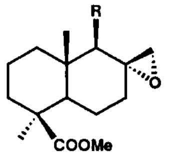
Series 8A

R^1=Me: 8A-59, -60
R^1=H: 8A-61



Series 8B

SERIES 9



SERIES 10

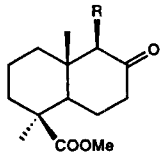


Figure 1. (continued)

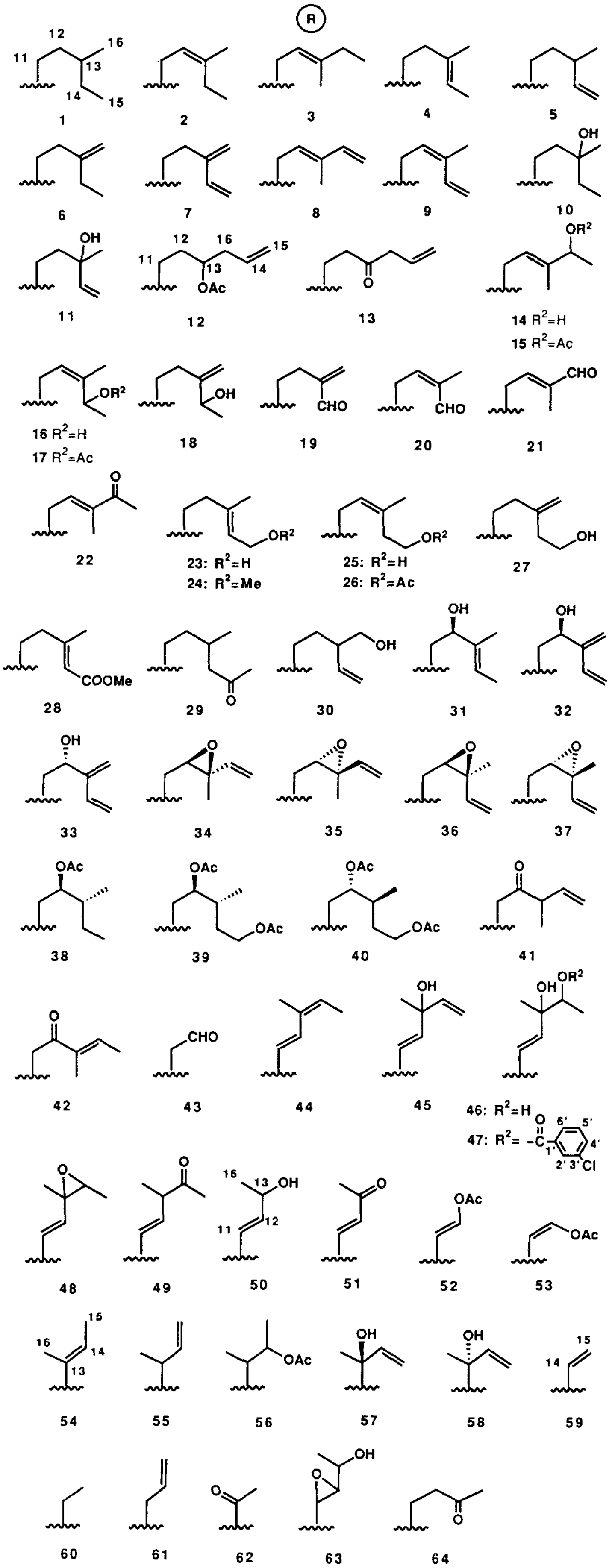


Figure 1. Labdane diterpenoids of series **1** to **10**.

Table 1. ^{13}C NMR data of labdane diterpenoids of series 1 to 10[a]

Series	Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	Others
1A	1A-1[b]	39.21	20.03	38.37	44.32	58.50	26.32	38.85	148.39	56.79	40.34	21.26	35.85	35.00	29.18	11.37	19.10	106.25	28.82	177.70	12.57	51.02	
														35.17	29.76		19.42						
	1A-2[c]	39.21	19.88	38.24	44.27	56.30	26.08	38.60	148.15	56.81	40.14	22.24	124.46	136.30	24.91	12.41	22.78	107.34	28.81	177.69	12.57	51.05	
	1A-3[c]	39.27	20.01	38.28	44.31	56.31	26.09	38.62	148.25	56.64	40.15	22.75	123.58	136.08	32.38	12.81	16.02	107.35	28.86	177.82	12.62	51.02	
	1A-4[b]	39.20	20.03	38.32	44.31	56.44	26.32	38.62[e]	148.20	55.57	40.25	22.29	38.79[e]	136.30	118.07	13.27	15.66	106.30	28.82	177.72	12.63	51.02	
	1A-5[b]	39.23	20.03	38.32	44.31	56.32	26.31	38.84	148.24	56.50	40.36	21.36	35.82	[d]	144.69	112.18	20.54	106.30	28.82	177.65	12.59	51.02	
												21.48				112.60		106.42					
	1A-6[b]	39.04	19.85	38.16	44.18	56.23	26.18	38.64	147.99	55.48	40.10	21.98	34.97	151.89	28.68	12.26	107.21	106.16	28.68	177.52	12.49	50.87	
	1A-7[b]	38.85	19.79	38.07	43.96	56.14	26.07	38.57	147.66	55.60	39.94	22.33	30.10	146.66	138.84	112.76	115.21	106.16	28.52	177.70	12.39	50.60	
	1A-8[c]	39.27	19.96	38.21	44.26	56.23[e]	26.01	38.49	147.97	56.36[e]	40.13	23.25	133.88	133.39	141.55	109.85	11.79	107.54	28.81	177.69	12.61	51.11	
	1A-9[b]	39.08	19.75	38.03	44.04	56.08	25.80	38.32	147.55	56.50	39.95	22.05	133.57	131.18	131.30	112.85	19.39	107.47	28.53	177.02	12.40	50.67	
	1A-10[b]	39.21	19.98	38.30	44.34	56.43	26.30	38.83	148.24	56.83	40.57	17.78	40.57	73.20	34.13	8.20	26.30	106.40	28.82	177.72	12.57	51.08	
															34.44								
	1A-11[c]	39.14	19.92	38.23	44.27	56.35	26.22	38.73	148.06	56.47	40.43	17.87	41.36	73.44	145.06	111.52	27.62	106.42	28.78	177.71	12.50	51.07	
									148.14	56.57			41.41	73.54	145.24	111.61	28.01	106.55					
	1A-12[c]	39.15[e]	19.97	38.26	44.31	56.32	26.23	38.71	147.85	55.58	40.25	19.32	32.55	73.38	133.77	117.54	38.91[e]	106.38	28.82	177.71	12.49	51.10	
											40.31	19.45	32.79	73.98			39.04[e]	106.55					
	1A-13[c]	39.05	19.95	38.21	44.31	56.30	26.26	38.68	147.82	55.51	40.40	17.61	41.38	209.02	130.70	118.65	47.87	106.42	28.84	177.66	12.45	51.11	
	1A-14[b]	38.97	19.68	37.92	43.98	55.98	25.74	38.26	147.74	56.15	39.83	22.17	124.95	137.62	72.70	21.26	11.18	107.13	28.49	177.26	12.32	50.74	
													125.06		72.81		11.35						
	1A-16[b]	38.94	19.62	37.88	43.95	55.96	25.72	38.23	147.49	56.54	39.86	21.40	126.10	136.93	65.23	20.66	16.69	107.10	28.46	177.30	12.27	50.73	
												21.53	126.20	137.03	65.32	20.83		107.21					
	1A-19[c]	39.09	19.89	38.20	44.25	56.28	26.19	38.67	147.53	55.68	40.19	22.15	27.29	150.78	194.68		133.82	106.65	28.79	177.65	12.56	51.10	
	1A-20[c]	39.32	19.90	38.10	44.27	56.15	25.97	38.41	147.42	56.98	40.42	21.73	150.30	135.31	191.32		16.39	108.07	28.80	177.54	12.70	51.22	
	1A-21[b]	39.42	19.96	38.10	44.33	56.25	25.95	38.36	147.69	55.88	40.19	24.49	155.87	138.98	195.02		9.60	107.07	28.82	177.60	12.68	51.17	
	1A-22[c]	39.36	19.93	38.16	44.28	56.22	25.94	38.39	147.88	55.92	40.14	24.54	144.97	137.18	199.69	25.37	11.30	107.74	28.83	177.60	12.66	51.19	
	1A-23[b]	39.01	19.84	38.08	44.20	56.20	26.13	38.31	147.83	55.44	40.06	21.87	38.60	139.56	123.31	59.04	16.12	106.23	28.64	177.54	12.45	50.90	
	1A-24[b]	39.19	19.97	38.30	44.33	56.43	26.27	38.49	148.06	55.62	40.24	22.05	38.78	140.86	120.56	69.01	16.47	106.35	28.81	177.65	12.58	51.02	MeOH 57.71
	1A-25[c]	39.22	19.95	38.19	44.27	56.25	26.07	38.57	148.06	56.79	40.18	22.52	128.77	130.56	35.27	60.51	23.29	107.40	28.82	177.75	12.58	51.12	
	1A-27[c]	39.26	19.96	38.24	44.30	56.32	26.27	38.75	148.04	55.71	40.26	21.95	34.17	146.59	34.17	60.35	11.43	106.32	28.81	177.76	12.61	51.13	
	1A-28[b]	39.18	19.97	38.21	44.37	56.33	26.22	38.72	147.76	55.44	40.29	21.72	39.77	160.83	115.05	167.25	18.81	105.44	28.78	177.61	12.58	51.07	15-MeO 50.69
	1A-29[c]	39.17	19.95	38.24	44.29	56.35	26.23	38.76	148.20	56.46	40.33	21.19	36.11	30.35	51.02	209.07	20.00	106.30	28.80	177.74	12.54	51.08	15-Me 29.98
	1A-30[c]	39.14	19.95	38.26	44.30	56.37	26.26	38.75	148.10	56.01	40.31	21.08	29.62	47.66	139.92	117.27	65.45	106.32	28.82	177.78	12.52	51.12	
		39.19							148.19		40.38	21.44	30.02		140.15	117.73	65.82	106.43					
	1A-31[c]	39.01	19.84	38.15	44.25	56.17	26.13	38.65	148.59	51.83	39.81	30.25	75.61	139.22	119.13	12.89	11.31	106.53	28.76	177.73	12.62	51.06	
	1A-32[c]	38.95	19.86	38.14	44.28	56.21	26.26	38.72	148.75	51.73	39.88	31.23	69.84	150.51	136.01	114.65	113.15	106.39	28.76	177.72	12.63	51.09	
	1A-33[c]	38.84	19.84	38.06	44.21	56.15	26.09	38.58	147.78	52.31	40.02	30.72	72.19	149.22	135.64	114.95[e]	114.78[e]	106.65	28.64	177.60	12.61	51.08	
	1A-34[c]	39.01	19.82	38.09	44.21	56.03	25.98	38.35	148.25	53.69	39.89	23.22	64.59	60.04	140.88	115.53	15.37	106.80	28.73	177.58	12.59	51.08	
	1A-35[c]	39.28	19.87	38.09	44.21	56.12	25.98	38.44	147.53	54.09	40.08	23.72	64.68	59.43	140.98	115.53	15.00	107.73	28.73	177.50	12.40	51.08	
	1A-36[c]	39.26	19.90	38.14	44.26	56.15	26.01	38.51	147.80	53.86	40.07	23.34	65.44	60.46	136.31	117.81	21.40	107.53	28.77	177.58	12.38	51.13	
	1A-37[c]	38.98	19.87	38.13	44.25	56.08	26.04	38.41	148.33	53.78	40.01	22.80	65.43	61.20	136.54	117.68	21.36	106.83	28.76	177.63	12.62	51.09	
	1A-41[b]	39.14	19.78	37.92	44.19	55.92	25.72	38.07	148.47	50.01	39.37	37.08	210.28	50.97	137.83	116.54	15.88	105.88	28.64	177.43	12.81	51.11	
									148.83	50.19		37.26		51.76	137.97	116.67	16.00	106.29					
	1A-43[c]	39.41	19.80	37.90	44.22	55.97	25.64	38.08	147.97	50.22	39.46	39.83	203.33					108.05	28.71	177.45	12.84	51.22	
	1A-44[b]	40.93	19.79	38.54	44.31	56.31	25.21	37.32	149.87	61.03	39.53	127.44	129.59	132.69	123.07	12.98	20.72	107.93	28.76	177.65	13.38	51.07	
	1A-45[c]	40.61	19.67	38.25	44.13	55.66	25.04	37.17	149.49	59.82	39.25	126.18	138.53	73.16	144.14	111.96	28.01	107.82	28.64	177.60	13.20	51.08	
												126.27	138.59		144.20								
	1A-46[b]	40.87	19.78	38.35	44.25	55.80	25.15	37.28	149.64	60.34	39.31	128.31	135.18	75.39	74.14	17.95	24.76	107.99	28.74	177.61	13.33	51.14	
	1A-48[b]	40.56	19.69	38.27	44.17	55.69	25.09	37.22	149.19	60.31	39.17	130.69	131.19	59.99	61.28	14.14	22.13	107.94	28.66	177.49	13.21	51.02	
		40.77							149.48					61.45			22.30						
	1A-49[b]	40.80	19.77	38.33	44.25	55.76	25.13	37.27	149.60	60.23	39.50	131.00	131.89	51.16	209.40	28.01	16.13	107.86	28.73	177.66	13.34	51.16	
	1A-50[b]	40.72	19.75	38.37	44.27	55.79	25.18	37.29	149.46	59.81	39.28	127.86	137.41	68.81			23.59	107.82	28.73	177.67	13.23	51.14	
												127.98											
	1A-51[b]	40.90	19.58	38.16	44.16	55.39	24.94	37.11	148.02	60.00	39.68	145.82	133.70	197.73			27.15	108.57	28.66	177.34	13.41	51.16	
	1A-52[c]	40.66	19.62	38.23	44.19	55.61	25.03	37.09	149.19	55.18	39.58	112.08	136.34					108.11	28.65	177.58	12.95	51.14	12-AcO: 167.96, 20.65
	1A-53[c]	39.81	19.62	38.23	44.19	55.56	25.03	37.09	148.06	51.31	39.21	111.16	134.93					107.73	28.65	177.58	12.59	51.14	12-AcO: 167.96, 20.79
1B	1B-9[c]	39.17	19.40	42.13	33.57	55.38	24.24	38.12	148.61	57.36	39.61	22.07	133.91	131.50	131.88	113.11	19.75	107.58	33.64	21.78	14.45		
	1B-11[c]	39.03	19.35	42.16	33.52	55.54	24.39	38.32	148.60	57.29	39.83	17.67	41.40	73.55	145.25	111.51	27.57	106.44	33.59	21.68	14.40		
	1B-44[c]	40.82	19.15	42.34	33.58	54.83	23.44	36.80	150.50	61.77	39.07	127.93	129.29	132.78	122.92	13.01	20.78	107.87	33.58	21.96	15.03		

2A	**2A-8**[c]	36.90	19.49	37.68	43.82	53.58	20.83	34.43	127.76	138.25	39.43	26.95	134.36	133.81	141.55	109.91	11.69	19.57	28.39	178.01	17.54	51.02	
	2A-9[c]	36.92	19.42	37.60	43.77	53.53	20.76	34.33	127.69	138.21	39.46	25.92	133.61	130.51	131.87	113.16	19.42	19.53	28.33	178.06	17.50	51.02	
	2A-15[c]	36.82	20.81	37.66	43.79	53.50	20.81	34.43	127.75	138.08	39.41	26.20	128.60	132.55	75.52	18.99	11.86	19.47	28.36	178.13	17.45	51.01	14-AcO: 170.36, 21.32
	2A-16[c]	36.78	19.10	37.45	43.56	53.36	20.40	34.19	127.22	138.40	39.30	25.38	126.76	136.19	65.24	20.62	16.65	19.33	28.13	177.73	17.36	50.73	
													126.93										
2B	**2B-44**[c]	38.34	19.07[e]	41.82	33.36	51.34	18.92[e]	33.66	126.87	141.97	38.10	126.55	130.56	133.15	123.19	13.02	20.42[f]	21.60	33.23	21.39	20.27[f]		
2C	**2C-14**[c]	36.33	19.35	37.45	43.43	46.95	30.21	70.20	128.41	143.90	40.05	26.23	124.76	137.76	73.24	21.59	11.58	17.43	28.22	177.93	15.93	51.17	
3	**3-9**[c]	39.67	18.86	42.21	32.97	50.14	23.71	122.57	135.17	55.32	36.82	25.30	133.95[e]	130.49	133.67[e]	113.13	19.80	22.69	33.28	21.96	14.02		
	3-44[c]	40.31	18.70	42.47	33.08	49.84	23.76	121.80	133.79	60.39	36.28	129.65[e]	129.85[e]	132.74	122.58	13.05	20.78	22.77	33.30	22.05	14.77		
4	**4-2**[c]	39.84	19.09[e]	38.20	43.92	57.54	18.96[e]	35.01	29.57	54.01	38.61	24.12	124.08	136.98	24.80	12.82	22.93	15.12	28.84	178.10	14.24	51.08	
	4-3[c]	39.88	19.07[e]	38.20	43.91	57.52	18.97[e]	35.04	29.69	53.72	38.60	24.45	122.94	136.75	32.53	15.97	12.89	15.17	28.84	178.10	14.24	51.07	
5	**5-7**[c]	39.30	19.22[e]	38.09	43.88	57.17	19.01[e]	29.30	39.25	52.52	38.26	24.21	30.17	146.70	138.81	113.25	115.48	61.12	28.77	177.91	13.89	51.16	
	5-9[c]	39.40	19.22[e]	38.07	43.84	57.11	19.10[e]	29.29	39.87	53.69	38.26	23.58	133.41	132.80	130.64	113.78	19.94	61.06	28.73	177.86	13.84	51.13	
	5-26[c]	39.34	19.15[e]	38.07	43.80	57.03	18.96[e]	29.67	35.34	53.44	38.17	23.93	126.92	131.58	31.08	62.66	23.63	63.49	28.70	177.73	13.87	51.21	15,17-AcO: 170.98, 171.32, 21.00
	5-38[c]	39.22	19.08[e]	38.05	43.88	56.98	18.86[e]	29.93	35.23	48.29	37.88	27.46	74.97	39.22	25.61	11.79	14.16	63.56	28.65	177.74	13.83	51.23	12,17-AcO: 171.06, 171.31, 21.07, 21.14
	5-39[c]	39.20	19.05[e]	38.00	43.84	56.94	18.81[e]	20.89	35.25	48.23	37.87	26.88	74.61	34.19	31.49	62.69	14.54	63.60	28.62	177.67	13.82	51.22	12,15,17-AcO: 170.92, 171.02, 171.24, 20.93, 21.03, 21.09
	5-40[c]	39.15	19.01[e]	37.94	43.79	56.82	18.77[e]	29.70	36.86	49.76	38.33	27.09	76.52	32.45	31.71	62.58	13.70	63.61	28.61	177.62	13.83	51.26	12,15,17-AcO:170.78, 170.98, 171.34, 20.90, 21.03, 21.11
6A$_1$	**6A$_1$-7**[c]	39.84	19.01	37.89	43.83	56.72	22.07	44.60	73.88	60.94	39.46	24.67	35.02	147.33	138.74	113.47	115.57	23.63	28.72	177.59	12.87	51.14	
	6A$_1$-18[c]	39.78	18.98	37.87	43.81	56.65	22.01	44.25	73.99	60.51	39.44	24.50	35.42	154.19	70.39	22.36	108.93	23.65	28.70	177.62	12.90	51.15	
	6A$_1$-42[c]	39.43	18.95	37.79	43.84	58.47	22.22	44.70	72.79	55.19	38.99	32.79	202.73	138.29	136.61	11.53	14.76	22.75	28.66	177.63	13.31	51.18	
6A$_2$	**6A$_2$-9**[c]	40.09	18.56	41.82	33.24	56.07	20.26	43.98	74.15	62.13	38.92	23.09	133.84[e]	130.76	133.58[e]	113.66	19.87	24.41	33.46	21.54	15.41		
	6A$_2$-44[c]	40.95	18.47	41.88[e]	33.32	55.88	20.06	42.00[e]	71.83	66.77	37.54	125.46	132.43	132.29	124.30	13.11	20.72	25.28	33.41	21.60	15.93		
6B	**6B-9**[b]	39.74	18.87	38.07	43.90	56.75	19.76	42.78	72.89	59.03	39.32	23.22	134.49	130.50	133.85	113.28	19.76	30.96	28.70	177.70	13.18	51.13	
	6B-11[c]	39.39	19.40	38.05	43.83	56.65	19.68	42.25	72.92	58.19	39.29	18.75	46.05	73.46	144.82	111.84	27.49	30.56	28.62	177.79	12.97	51.15	
															144.92	111.94	27.53						
	6B-14[c]	39.52	18.73	37.92	43.76	56.58	19.61	42.55	72.70	58.79	39.05	23.22	128.23	136.32	73.07	21.49	11.76	30.77	28.57	177.74	13.06	51.07	
	6B-15[c]	39.70	18.86	38.03	43.90	56.65	19.73	42.75	72.83	58.73	39.20	23.41	131.01	132.25	75.55	18.93	12.04	30.85	28.72	177.85	13.20	51.20	14-AcO: 170.33, 21.36
7A$_1$	**7A$_1$-54**[c]	39.87[e]	13.86	42.43	33.05	57.31	20.51	39.73[e]	80.65	59.65	36.22	27.87	80.47	136.78	119.68	11.73	12.97	21.46	33.51	21.09	14.86		
	7A$_1$-55[c]	39.90[e]	18.40	42.47	33.07	57.32	20.54	39.73[e]	80.72	59.39	36.21	25.32	79.01	42.74	140.75	114.45	15.66	21.44	33.54	21.12	14.85		
									80.62	59.53		25.40	79.26	42.93	140.91	114.28	15.29	21.34					
	7A$_1$-57[c]	39.74[e]	18.31	42.39	33.03	57.24	20.52	39.57[e]	81.41	60.20	36.29	23.97	81.58	74.46	143.06	112.90	23.39	21.21	33.50	21.07	14.73		
	7A$_1$-58[c]	39.73[e]	18.33	42.41	33.06	57.24	20.54	39.63[e]	81.47	60.13	36.29	24.29	81.66	74.55	141.19	113.58	24.87	21.40	33.51	21.09	14.77		
7A$_2$	**7A$_2$-54**[c]	40.69[e]	18.36	42.43	33.08	57.12	20.51	40.08[e]	80.65	61.03	36.28	28.44	82.91	136.78	117.92	12.63	14.86	24.85	33.51	21.03	15.79		
	7A$_2$-57[c]	40.81[e]	18.41	42.47	33.06	57.07	21.40	40.10[e]	81.24	60.99	36.40	24.38	85.40	73.24	141.04	113.44	25.91	25.48	33.51	20.97	15.88		
	7A$_2$-58[c]	40.79[e]	18.40	42.39	33.09	57.02	21.37	40.11[e]	81.27	60.69	36.35	23.97	85.18	73.14	144.22	112.49	23.19	25.34	33.50	20.95	15.90		
7B	**7B-54**[c]	41.89	19.10	38.14	43.78	53.89	19.73	36.73	81.66	57.77	36.39	32.75	81.56	133.67	116.00	12.79	12.96	31.40	28.60	177.62	14.59	51.14	
	7B-56[b]	41.85	19.15	38.19	43.79	54.04	19.91	36.98	81.75	57.42	36.20	33.36	79.67	45.01	72.10	13.97	10.12	31.62	28.69	178.06	14.55	51.19	14-AcO: 170.37, 21.48
8A	**8A-59**[c]	39.22	19.03	38.06	43.79	56.77	21.44	43.11	74.69	54.97	37.37	15.37	35.58	73.17	147.85	110.27	28.56	24.98	28.60	177.70	12.93	51.07	
	8A-60[c]	39.46	19.13	38.18	43.87	56.84	21.41	42.98	74.16	57.77	37.36	15.55	37.89	72.94	35.80	8.00	27.40	24.75	28.59	177.77	13.25	51.09	
	8A-61[c]	39.39	19.15	38.14	43.86	56.84[e]	21.49	41.90[e]	74.48	56.99[e]	37.21	18.54	32.90	68.96	135.39	116.21	41.30[f]	20.26	28.65	177.79	13.17	51.12	
8B	**8B-60**[c]	39.46	19.13	38.18	43.87	56.84	21.54	43.51	74.46	57.19	37.35	15.49	36.92	73.52	33.37	9.00	29.56	23.70	28.59	177.77	13.19	51.09	
	8B-62[c]	39.55	19.10	38.04	43.81	56.75	21.53	42.84	76.83	57.27	37.25	16.17	32.88	78.40	214.01	20.72	28.36	24.26	28.62	177.58	13.38	51.16	
9	**9-47**[c]	40.56	19.21	37.99	44.01	55.22	23.15	36.07	58.24	57.45	39.47	123.09	138.65	71.19	76.88	14.70	25.24	50.33	28.77	177.52	13.59	51.32	1′: 132.08, 2′: 129.68, 3′: 134.49, 4′ 133.02, 5′: 129.57, 6′: 127.77, CO: 164.92
													138.78	74.34	77.37	15.06	24.58						
	9-63[b]	42.23	19.27	37.84	43.89	55.08	23.26	36.21	58.93	60.49	40.40	65.15	66.06	51.99			20.30	50.63	28.75	177.30	14.42	51.35	
10	**10-18**[c]	39.43	19.68	38.00	44.34	55.00	25.70	43.09	211.33	62.71	43.53	20.24	27.37	150.21	194.74		134.38		28.79	177.10	13.09	51.37	
	10-43[c]	39.47	19.46	37.78	44.17	54.41	24.86	41.82	209.68	56.96	41.95	37.09	200.99						28.66	176.88	13.53	51.34	
	10-64[c]	39.33	19.67	37.94	44.30	54.00	25.57	43.04	211.64	62.13	43.55	16.32	42.62	208.99			29.86		28.79	177.01	13.00	51.31	

[a] δ in ppm downfield from TMS in $CDCl_3$ solutions. [b] 20 MHz. [c] 75 MHz. [d] Signal not observed. [e,f] Signals with the same letter may be interchanged.

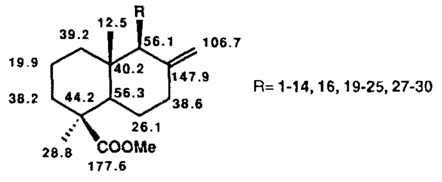


Figure 2. Averaged δ values for compounds of series **1A**.

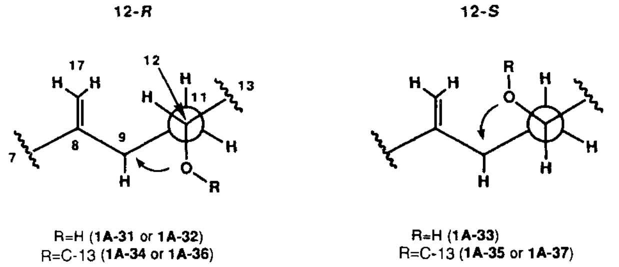


Figure 3. Preferred conformations of the side-chains of 12-oxygenated $\Delta^{8(17)}$-labdanes.

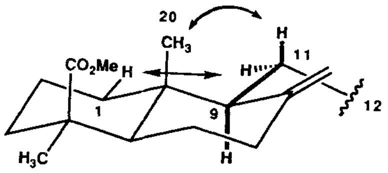


Figure 4. Shielding interactions between C-1, C-11 and C-20, and *anti*-disposition of H-11β and H-9 in $\Delta^{8(17)}$-labdanes with a saturated C-11—C-12 bond.

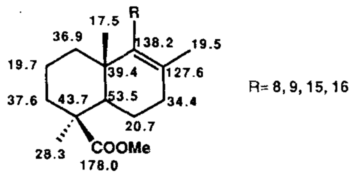


Figure 5. Averaged δ values for compounds of series **2A**.

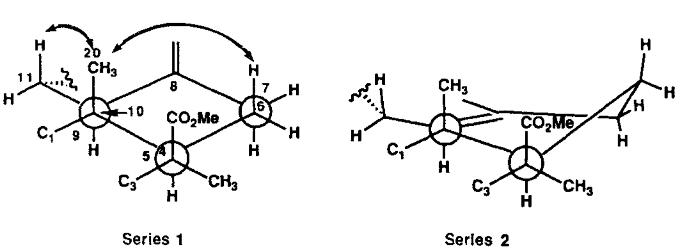


Figure 6. Increase in the C-20—C-11 dihedral angle and decrease in the C-1—C-11 dihedral angle from series **1** to series **2**.

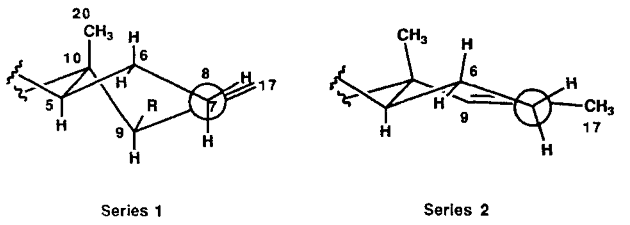


Figure 7. Decrease in the C-6—C-9 dihedral angle from series **1** to series **2**.

Table 2. δ Changes ($\Delta\delta$) from series 1A to series 1B[a]

Carbon	$\Delta\delta$ (1B) − (1A)[b]	Effect
2	−0.5	γ
3	+4.0	β
4	−10.5	α
5	−0.8	β
6	−1.8	γ
9	+1.0	δ
18	+4.9	β
20	+1.9	δ

[a] **1B-9** and **1B-11**.
[b] +, Deshielding; −, shielding.

methoxycarbonyl group, which prefers to eclipse the C-3—C-4 bond,[21] induces a deshielding of *ca.* 2 ppm on C-20 as a consequence of the enhanced *syn*-axial interactions between the two methyl groups. The same argument supports the shielding (of *ca.* 2 ppm) of C-6, in this case by increasing the γ-*gauche* effect between 4β-Me and H-6β (this effect seems to be weaker on C-2). The presence of a Δ^{11} double bond (**1B-44**) modifies the corresponding decalin carbons in the same way as in series **1A**.

Series 2

The change of the $\Delta^{8(17)}$ exocyclic double bond (series **1**) to the Δ^{8} endocyclic position (series **2**) introduces a considerable modification of the ring B conformation causing important shift changes of the decalin carbons, as shown in Fig. 5 and Table 3. The greater flatness of ring B in series **2** explains the observed deshielding at C-20, because the γ-*gauche* effects from H-11β and, to a lesser extent from H-6β, have been weakened (Fig. 6). In the same way, the considerable decrease in the C-6—C-9 dihedral angle could explain the observed shielding of C-6 (Fig. 7). On the other hand, the shielding of *ca.* 4 ppm of C-7 could be attributed to the γ-*syn* periplanar arrangement with respect to C-10.[22] In addition to these two arguments, the deviation from the H-6β/H-7α *anti* disposition in series 1, as a result of the new half-chair conformation of ring B, must also contribute to the shielding of C-6 and C-7. The observed shielding of C-1 and C-5 may be explained by their new homoallylic positions[23] in addition to the decreasing C-1—C-11 and C-5—C-8 dihedral angles (Fig. 8). As for C-11, the deshielding of *ca.* 4 ppm (i.e. **2A-9** compared with **1A-9**) is the balance of its deshielding allyl position and the γ-*syn* periplanar situation with respect to C-17 and the

Table 3. δ Changes ($\Delta\delta$) from series 1A to series 2A

Carbon	$\Delta\delta$ (2A) − (1A)
1	−2.3
5	−2.8
6	−5.4
7	−4.2
20	+4.9

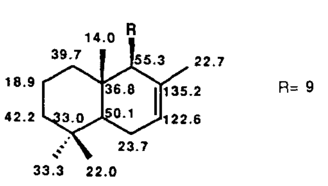


Figure 8. δ Values for compound 3–9.

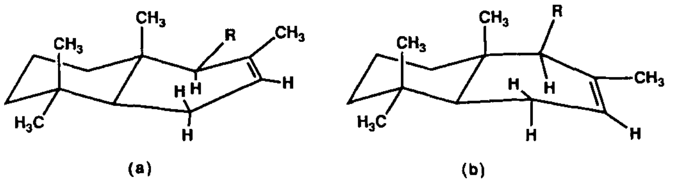


Figure 9. Conformations of ring B for compounds of series 3.

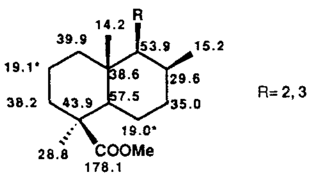


Figure 10. Averaged δ values for compounds of series 4.

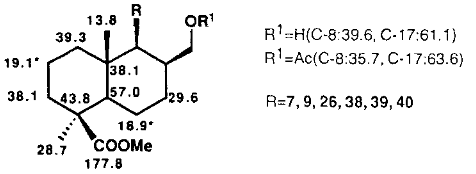


Figure 11. Averaged δ values for compounds of series 5.

loss of the H-9/H-11β *anti* interaction. The $\Delta\delta$ values outlined in Table 3 can be applied to predict the assignments of **2B-44**, taking as reference those of **1B-44**. Finally, the α disposition of HO—C-7 in **2C-14** has been mainly established by the considerable shielding of C-5 (-6.5 ppm) as opposed to that expected for 7β-hydroxy derivatives.[15]

Series 3

As stated for series **2**, the half-chair conformation of ring B introduces important differences in this series compared with series **1**. The comparison of the δ values of compound **3-9** (Fig. 8) with those of **1B-9** (Table 1) reveals shift changes at C-5, C-9, C-10 and C-11, according to some well established 2D NMR examples[18,19] (Table 4). However, the δ value of C-6 scarcely changes, as both the γ-*syn* periplanar effect from C-9 and the α-effect from C-8 mutually cancel. The location of C-6 and C-9 in the same plane produces an increase of the γ interaction between C-7 and C-10 ($\Delta\delta$ -2.8 for C-10), and between C-8 and C-5 ($\Delta\delta$ -5.2 for C-5). The larger shielding of C-5 with respect to C-10 can be explained by its homoallylic position. The disposition of the H-11 hydrogens and C-1, C-20 carbons should be similar to that presented in series **1**, since the C-1 and C-20 δ values in series **3** do not suffer appreciable modifications. This fact seems to suggest that the conformation depicted in Fig. 9(a) is the most probable for ring B as the dihedral C-1—C-11 and C-11—C-20 angles are closest to those of series **1**.

Table 4. δ Changes ($\Delta\delta$) from series 1B to series 3

Carbon	$\Delta\delta$ (3-9) – (1B-9)
5	−5.2
9	−2.0
10	−2.8
11	+3.2

Table 5. δ Changes ($\Delta\delta$) from series 1A to series 4

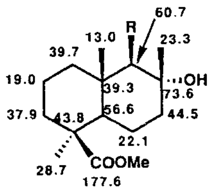
Carbon	$\Delta\delta$ (4) – (1A)
6	−7.2
7	−3.6
9	−2.6
10	−1.6
20	+1.7

Series 4

The β disposition of the 8-Me in compounds **4-2** and **4-3** has been established by the chemical shift of C-17 (δ 15.2), being tpyical of the value of an axial methyl group on a cyclohexane with a vicinal equatorial alkyl group[13] (slightly deshielded by a δ-*syn* axial effect with the 10-Me), and by that of C-6, *ca.* 7 ppm upfield with respect to series **1A** because of the γ-*gauche* influence from C-17.[15] Figure 10 shows the δ values for this series and Table 5 shows the differences observed compared with series **1A**. Thus, both pairs, C-7, C-9 and C-6, C-10, suffer upfield shifts as a consequence of the loss of the allylic position and the appearance of the γ-*gauche* effect of the 8β-Me, respectively. The 1,3-diaxial disposition of the 8β-Me and 10-Me causes a deshielding of *ca.* 2 ppm on C-20.[24]

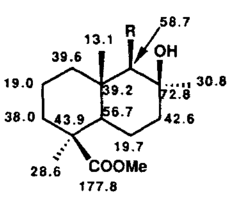
Series 5

The presence of an oxygenated functionality on C-17, either HO or AcO, is noted in the δ shifts of carbons α (C-17), β (C-8) and γ (C-7), with respect to series **4**, according to the substituent effects of these groups (Fig. 11). However, C-9 seems not to be affected by the OR group on C-17 (i.e. **5-9** *vs.* **4-2**), its δ value being dependent on the type of side-chain. Thus, the existence of a Δ^{12} (δ 53.44, **5-26**; δ 53.69, **5-9**), Δ^{13} (δ 52.52, **5-7**), (12*R*)-OAc (δ 48.29, **5-38**; δ 48.23, **5-39**) or (12*S*)-OAc (δ 49.76, **5-40**) is clearly observed. The similarity of the C-6 and C-20 chemical shifts in both series confirms the β disposition of C-17.



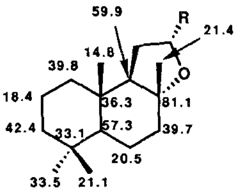
R= 7, 18

Figure 12. δ Values for compounds **6A$_1$-7** and **6A$_1$-18**.



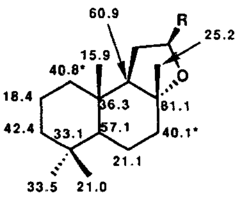
R=9, 11, 14, 15

Figure 13. Averaged δ values for compounds of series **6B**.



R=54, 55, 57, 58

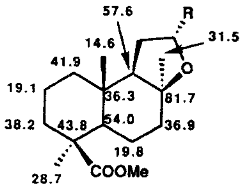
Series 7A$_1$



R=54, 57, 58

Series 7A$_2$

Figure 14. Averaged δ values for compounds of series **7A$_1$** and **7A$_2$**.



R=54, 56

Figure 15. Averaged δ values for compounds of series **7B**.

Table 6. δ Changes (Δδ) from series 1A to series 6A$_1$ and 6B

Carbon	Δδ (6A$_1$) − (1A)	Δδ (6B) − (1A)
2	−0.9	−1.0
6	−4.0	−6.4
7	+5.9	+4.0
9	+4.3	+2.6

Series 6

This series groups labdanes with 8α-OH (series **6A**) and 8β-OH (series **6B**). The comparison of the well established 2D NMR decalin δ values of series **6A$_1$** (Fig. 12) with those of series **1A** (Table 6) basically shows some differences at C-6, C-7 and C-9. As regards series **6A$_2$**, every chemical shift can be predicted by application of the data in Table 2 to the δ values of series **6A$_1$**. Using the assignments for series **6A$_1$** and taking into account the shielding expected (*ca.* 2 ppm) on carbons α, β and γ (with respect to OH) in *trans*-decalin systems, when the hydroxy group changes its equatorial position to an axial position,[15] we were able to assign series **6B**. Figure 13 and Table 6 summarize some characteristics of series **6B**. The two series **6A** and **6B** can be distinguished by the different chemical shifts of C-17 (δ 23.3, series **6A**; δ 30.8, series **6B**), according to the typical values of axial and equatorial methyl groups on oxygenated carbon.

Series 7

The assignments of the compounds of series **7A** have been accomplished by taking as reference the δ values assigned in the literature to compounds **7A$_1$-57** and **7A$_2$-58**.[17] The typical chemical shifts for series **7A$_1$** and **7A$_2$** are shown in Fig. 14. When series **7A$_1$** is compared with series **6A$_2$** (**6A$_2$-9**) several modifications are observed (Table 7); the shielding of C-7, C-9 and C-17 can be explained by the creation of a new γ-effect from C-12, whereas this carbon causes an upfield shift at C-8 from the β-effect. The slight change of the C-11—C-12 bond orientation associated with the ring C formation, with respect to that of $\Delta^{8(17)}$-labdanes,[16] seems not to affect the δ values of C-1 and C-20. However, the steric interaction between the side-chain and the 8β-Me in 12-(*S*) derivatives (series **7A$_2$**) is displayed by the shielding of C-1, C-9, C-17 and C-20 (Table 7). The study of series **7B** was assisted by 2D NMR experiments performed on **7B-54**. The δ values of the series and their deviation with respect to series **6B** are shown in Fig. 15 and Table 8, respectively. As can be appreciated, the Δδ shifts of series **7B** are slightly larger than those of **7A** (Table 7) owing to the enhanced deviation of the C-11—C-12 bond orientation with respect to series **6B**. This fact is reflected in the more deshielded C-1 and C-20 signals. In addition to some different δ values shown in Figs 14 and 15, the two series can be clearly distinguished by the resonance of C-17, δ 21.4 or 25.2 for series **7A**, and δ 31.5 for series **7B**.

Table 7. δ Changes (Δδ) from series 6A$_2$ to series 7A$_1$ and 7A$_2$ and comparison of series 7A$_1$ and 7A$_2$

Carbon	Δδ (7A$_1$) − (6A$_2$-9)	Δδ (7A$_2$) − (6A$_2$-9)	Δδ (7A$_2$) − (7A$_1$)
1	—	+0.7	+1.0
3	+0.6	+0.6	0
5	+1.3	+1.1	~0
6	—	+0.9	+0.6
7	−4.3	−3.9	< +0.5
8	+6.9	+6.9	0
9	−2.3	−1.2	+1.0
10	−2.0	−1.9	~0
17	−3.0	+0.9	+3.9
20	−0.6	+0.5	+1.1

Table 8. δ Changes (Δδ) from series 6B to series 7B

Carbon	Δδ (7B) − (6B)
1	+2.3
5	−2.7
7	−5.7
8	+8.9
9	−1.1
10	−2.9
17	+0.7
20	+1.5

Table 9. δ Changes (Δδ) from series 6A$_1$ to series 9

Carbon	Δδ (9) − (6A$_1$)
5	−1.4
6	+1.1
7	−8.4
9	−3.2

Table 10. δ Changes (Δδ) from series 1A to series 10

Carbon	Δδ (10) − (1A)
5	+1.8
7	+4.5
9	+6.8
10	+3.3

Series 8

Assignment of the manoyl oxides (series **8A**), manoyl 13-*epi*-oxides (series **8B**) and their derivatives have been performed according to bibliographic data[16,17] and the 2D NMR correlations performed on **8A-59**. The opposite configuration of C-13 in compounds **8A-60** and **8B-60** (Table 1) is reflected at C-14, C-15, C-16 and C-17. The C-13 stereochemistry was appropriately established since the carbon axially placed on C-13 must suffer a shielding shift (C-16 for **8A-60** and C-14 for **8B-60**). The deshielding exerted by either C-14 or C-16 on C-17 in both series is not observed in **8A-61** (δ_{17} : 20.26) as there is no axial substituent on C-13.

Series 9

The 8α,17-epoxide of series **9** is defined by the C-17 δ value (50.3 ppm), slightly deshielded with respect to that (*ca.* 48 ppm) of reported 8β,17-epoxy derivatives.[9] Because of the reduced axial nature of C-17 and equatorial nature of the oxygen attached to C-8 with respect to the methylcarbinol in series **6A**, several differences are observed for the decalin (Fig. 16 and Table 9).

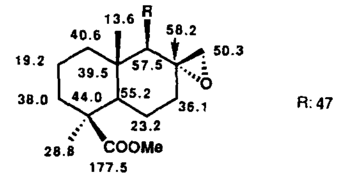


Figure 16. δ Values for compound **9-47**.

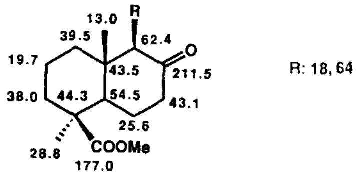


Figure 17. Averaged δ values for series **10**.

Series 10

The replacement of the methylene by an oxygen on the $\Delta^{8(17)}$ double bond of series **1** causes the corresponding δ changes associated with the functional group change according to the literature (Fig. 17 and Table 10).[9]

EXPERIMENTAL

^{13}C NMR spectra were recorded on Bruker WP 80 SY (20 MHz) and Bruker 300 AM (75 MHz) spectrometers operating in the pulsed Fourier transform (PFT) mode. All measurements were performed at a probe temperature of 300 K using solutions of the compounds in $CDCl_3$ (50–150 mg ml^{-1}) containing TMS as internal standard. The δ values were adjusted with respect to the $CDCl_3$ central peak at 77.00 ppm. For ^{1}H–^{1}H (300 MHz) and one-bond ^{1}H–^{13}C (300/75 MHz) 2D correlations, pulse sequences COSY.AUR[25] and XHCORRD.AUR[26] from the Bruker DISnmr 85 program library were used, respectively.

All the compounds were characterized by $[\alpha]_D$, MS, IR and ^{1}H NMR. The communic acids were isolated from berries of *Juniperus communis* L.[27] and studied as methyl ester derivatives (**1A-7**, **1A-8** and **1A-9**).[2] Compounds **1B-9**, **1B-44**, **3-9**, **3-44**, **6A$_2$-9** and **6A$_2$-44** were isolated from *Abies marocana*.[8] Methyl isocupressate (**1A-23**), its 15-*O*-methyl derivative (**1A-24**) and dimethyl agatate (**1A-28**) were isolated from previously methylated fractions obtained from the wood of *Juniperus oxycedrus* L.[2] The homolabdane **1A-29** was isolated from berries of *Juniperus oxycedrus* L. subsp. *macrocarpa*.[3] Catalytic hydrogenation of methyl *trans*-communate (**1A-8**) yielded **1A-1**, **1A-3**, **1A-4** and **1A-5**.[1] Compounds **1A-2** and **4-2** were obtained in the reaction of methyl *cis*-communate (**1A-9**) with diimide, whereas compounds **4-3** and **1A-6** were isolated from the same reaction with methyl *trans*-communate and methyl mirceocommunate (**1A-7**), respectively.[1] The oxymercuration–demercuration (OM–DM) reaction of **1A-7** yielded **1A-11**, **1A-12**, **1A-13**, **8A-61** and **8B-62** (when $NaBH_4$ was used as reducing agent) and **6A$_1$-7**,

6A$_1$-18, **6B-11** and **8A-59** [when Na(Hg) was used].[5] Compounds **1A-14**, **1A-16**, **1A-31**, **2A-8**, **2A-9**, **2A-15**, **2A-16**, **2C-14**, **6B-9**, **6B-14**, **6B-15**, **7B-54** and **7B-56** were formed in the OM–DM reaction of **1A-8** and **1A-9**.[7] The reaction of **1A-9** with $^1O_2$ afforded **1A-32**, **1A-33** and **1A-45**. The treatment of **1A-8** and **1A-9** with *m*-CPBA led to **1A-34**, **1A-35**, **1A-36** and **1A-37**, and the ring-opening reaction of these with BF_3–Et_2O at 0 °C yielded **1A-41** and **6A$_1$-42**, among other compounds.[6] In the ozonolysis reaction of **1A-7**, **1A-8** and **1A-9**, compounds **1A-43**, **1A-20**, **1A-21**, **1A-19**, **10-19** and **10-43** were formed. Compounds **1A-10**, **8A-60** and **8B-60** were obtained by OM–DM reaction of **1A-3** and **1A-22** by oxidation of **1A-14** with PDC.[1] Compounds **1A-25**, **1A-27**, **1A-30**, **5-9**, **5-7**, **5-26**, **5-38**, **5-39** and **5-40** were obtained in different hydroboration–oxidation reactions on **1A-7** and **1A-9**.[1] The thermal isomerization of **1A-9** yielded **1A-44**. The ozonolysis and subsequent reduction of **1A-44** yielded **1A-51** and **1A-50**, respectively, and the reaction of **1A-44** with *m*-CPBA afforded **1A-46**, **1A-48**, **1A-49** and **9-47**.[1] Similar reaction of **1A-50** with *m*-CPBA led to **9-63**.[1] The acetylation of **1A-43** using DMAP as catalyst provided a mixture of enol acetates **1A-52** and **1A-53**.[4] Compound **2B-44** was obtained in the reaction of compound **6A$_2$-44** with $POCl_3$, and compounds **7A$_1$-54**, **7A$_1$-55**, **7A$_1$-57**, **7A$_1$-58**, **7A$_2$-54**, **7A$_2$-57** and **7A$_2$-58** resulted from the OM–DM reaction of *cis*-abienol (**6A$_2$-9**).[1]

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