Electronic Supplementary Information

Structure elucidation of C_{80}, C_{81} and C_{82} isoprenoid tetraacids responsible for naphthenate deposition in crude oil production

Bjart F. Lutnaes, Jostein Krane, Ben E. Smith and Steven J. Rowland

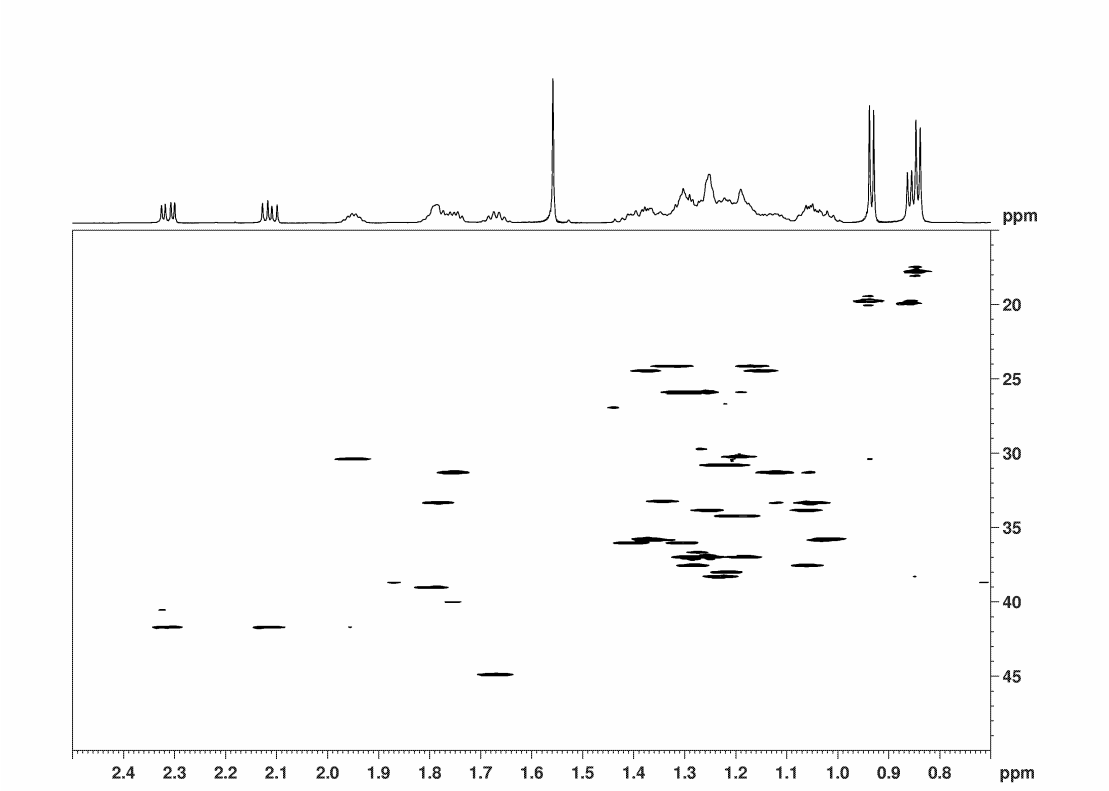

Fig. 1. HSQC spectrum (800 MHz, 298 K, $CDCl_3$) of the tetracyclic tetraacid (**3**).

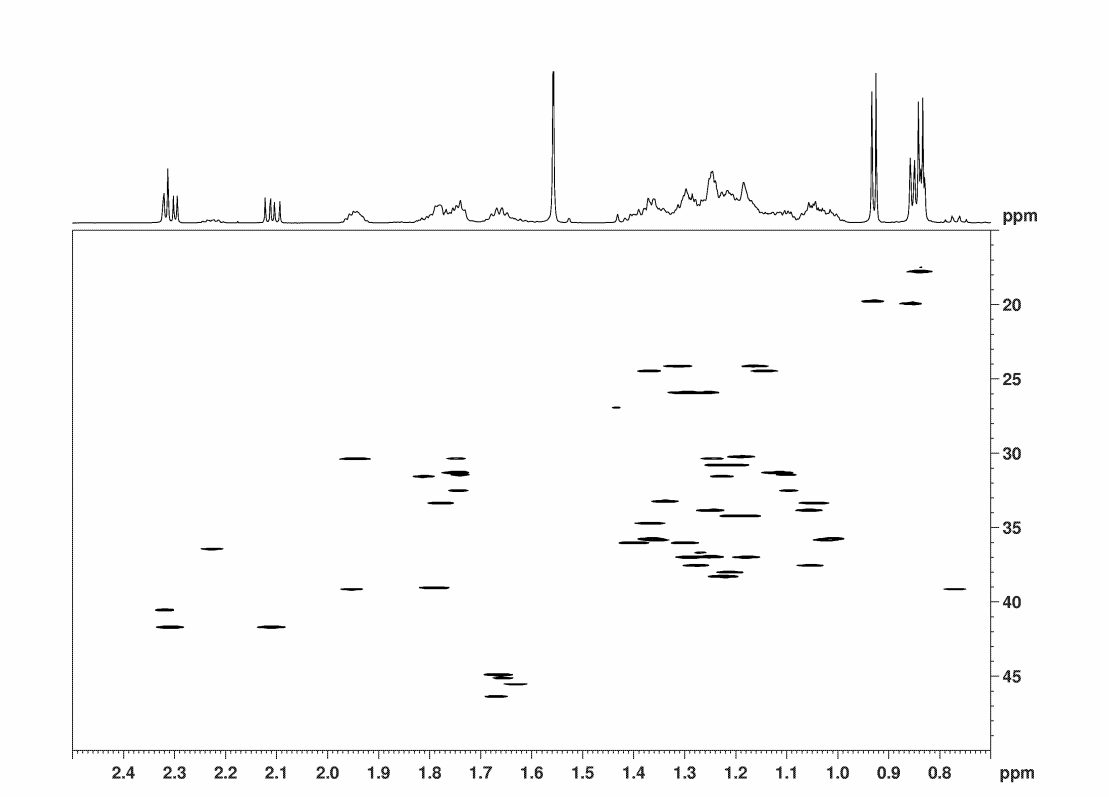

Fig. 2. HSQC spectrum (800 MHz, 298 K, $CDCl_3$) of the pentacyclic tetraacid present as two regioisomers (structures not given).

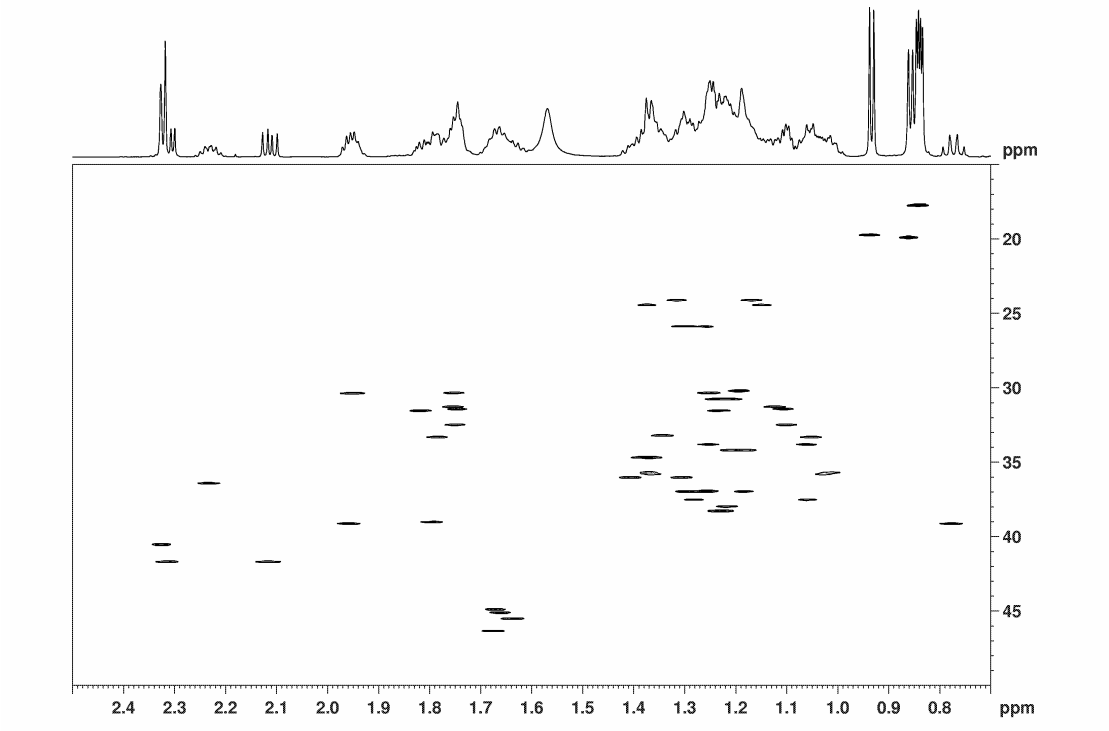

Fig. 3. HSQC spectrum (800 MHz, 298 K, $CDCl_3$) of the hexacyclic tetraacid (**2, 5-7**), present as four regioisomers.

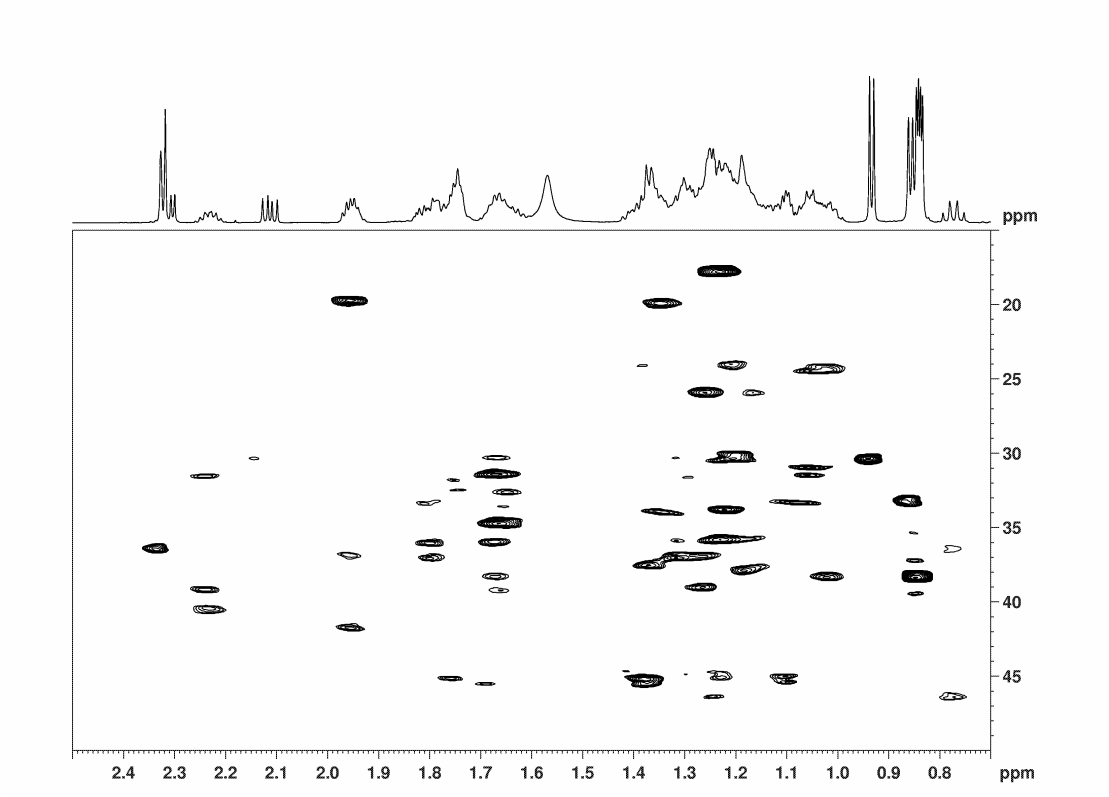

Fig. 4. H2BC spectrum (600 MHz, 298 K, $CDCl_3$) of the tetracyclic tetraacid (**2, 5-7**).

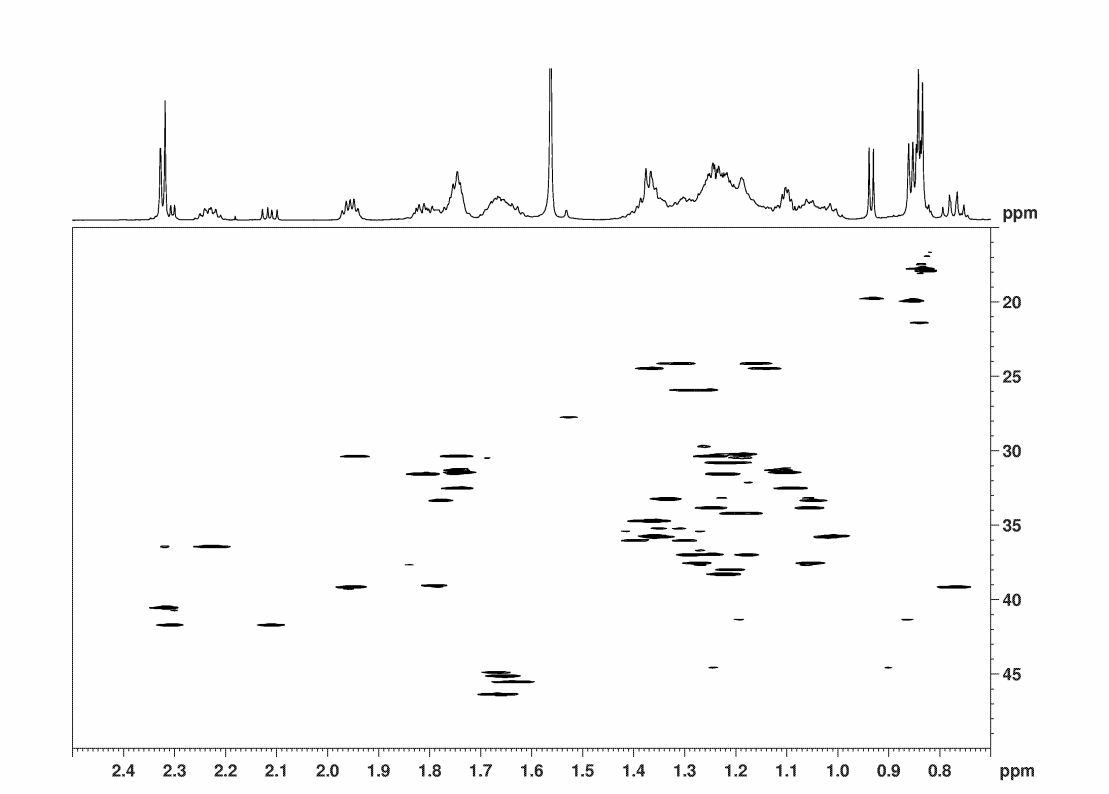

Fig. 5. HSQC spectrum (800 MHz, 298 K, $CDCl_3$) of the mixture of C_{80}, C_{81} and C_{82} heptacyclic tetraacids (structures not given). Regioisomers are possible.

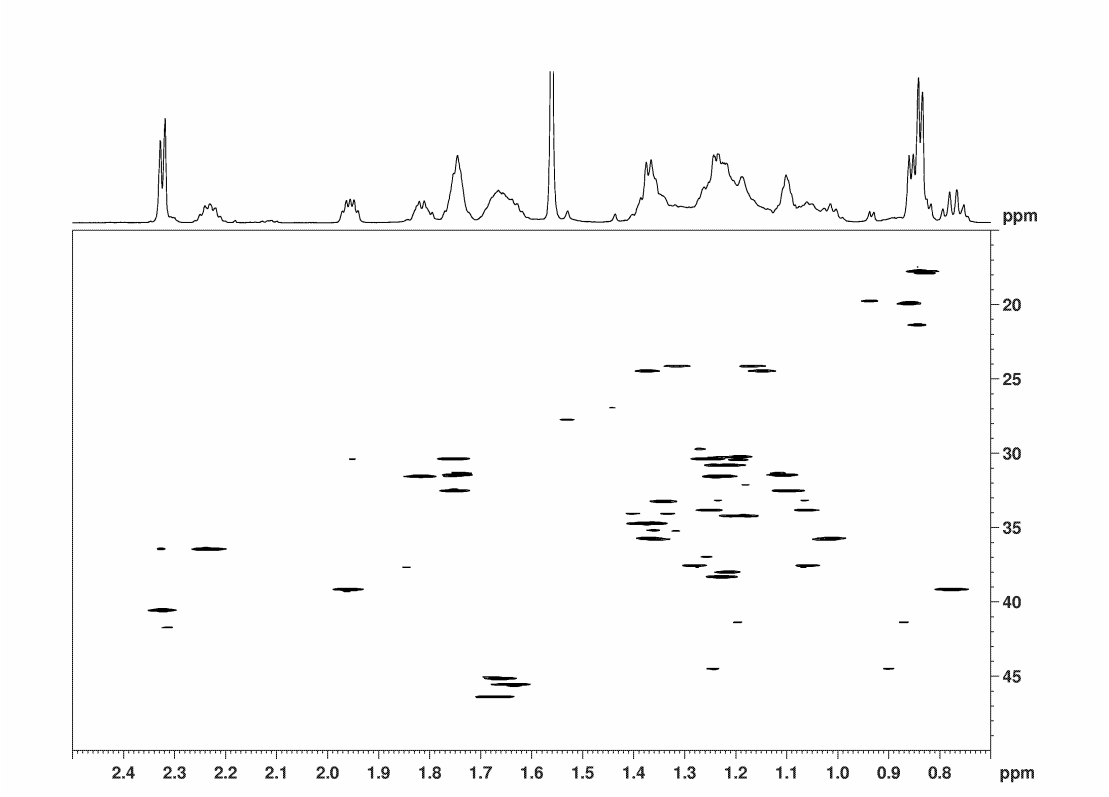

Fig. 6. HSQC spectrum (800 MHz, 298 K, $CDCl_3$) of the mixture of C_{80}, C_{81} and C_{82} octacyclic tetraacids (**4**, **8**, **9**).

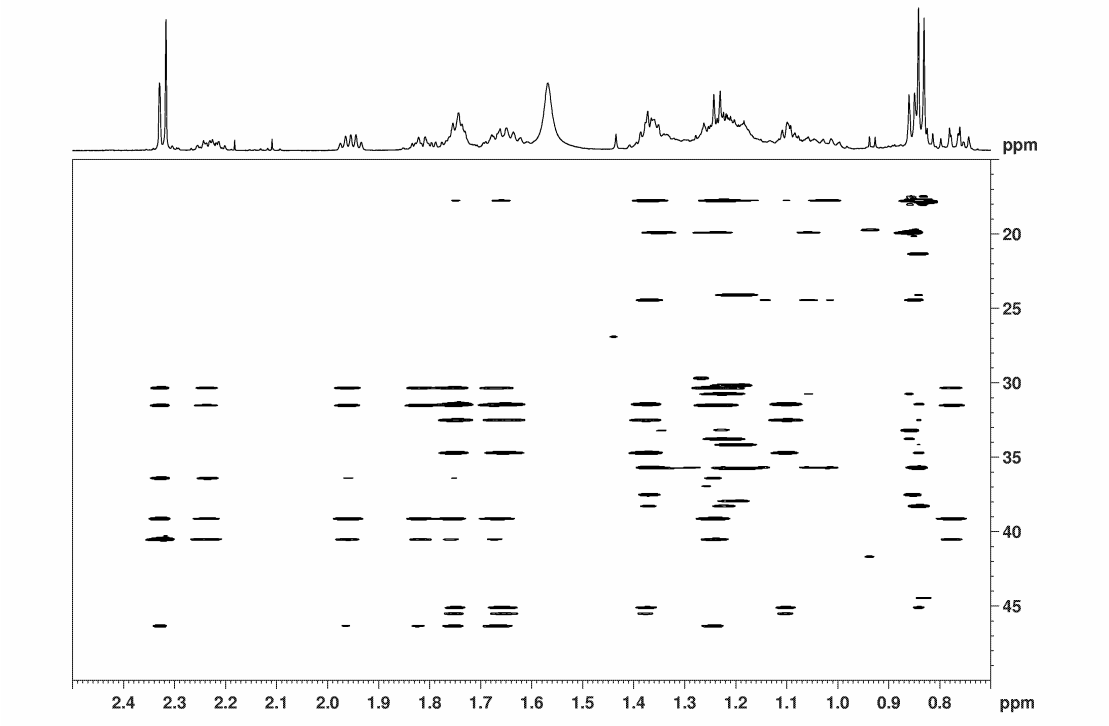

Fig. 7. 2D TOCSY-HSQC spectrum (600 MHz, 298 K, $CDCl_3$) of mixture of C_{80}, C_{81} and C_{82} octacyclic tetraacids (**4**, **8**, **9**).

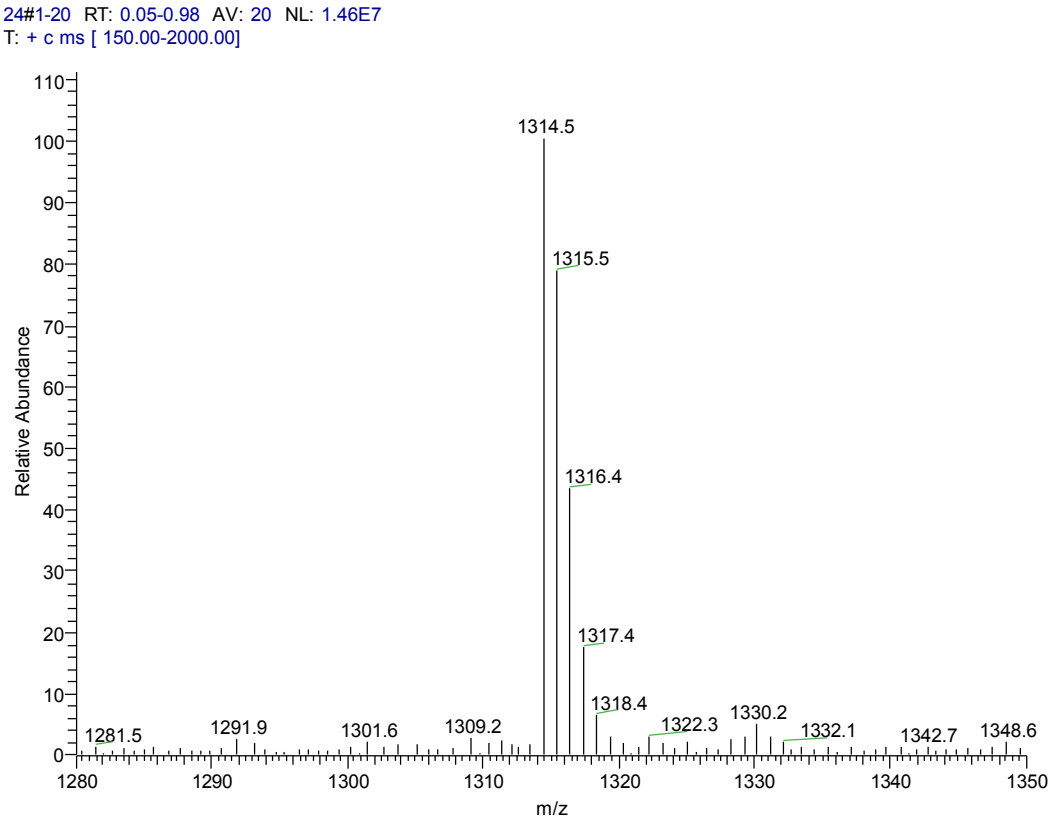

Fig. 8. ESI MS spectrum of the tetracyclic tetraacid (**3**).

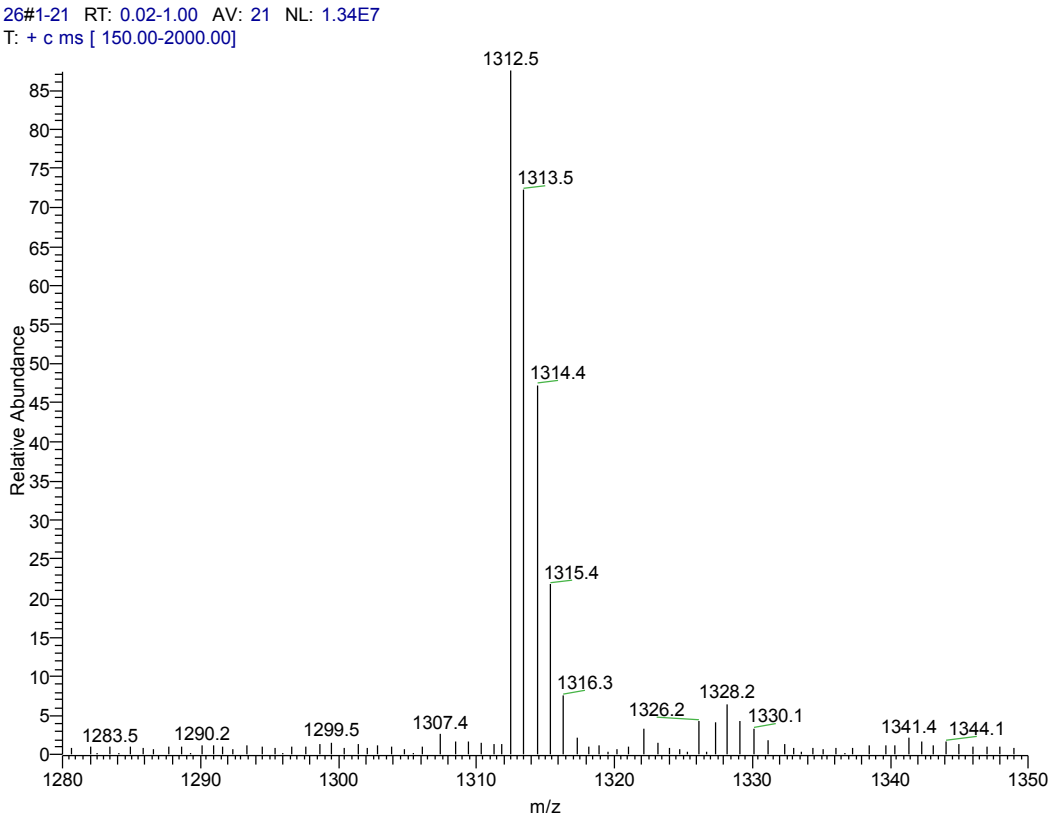

Fig. 9. ESI MS spectrum of the pentacyclic tetraacid present as two regioisomers (structures not given).

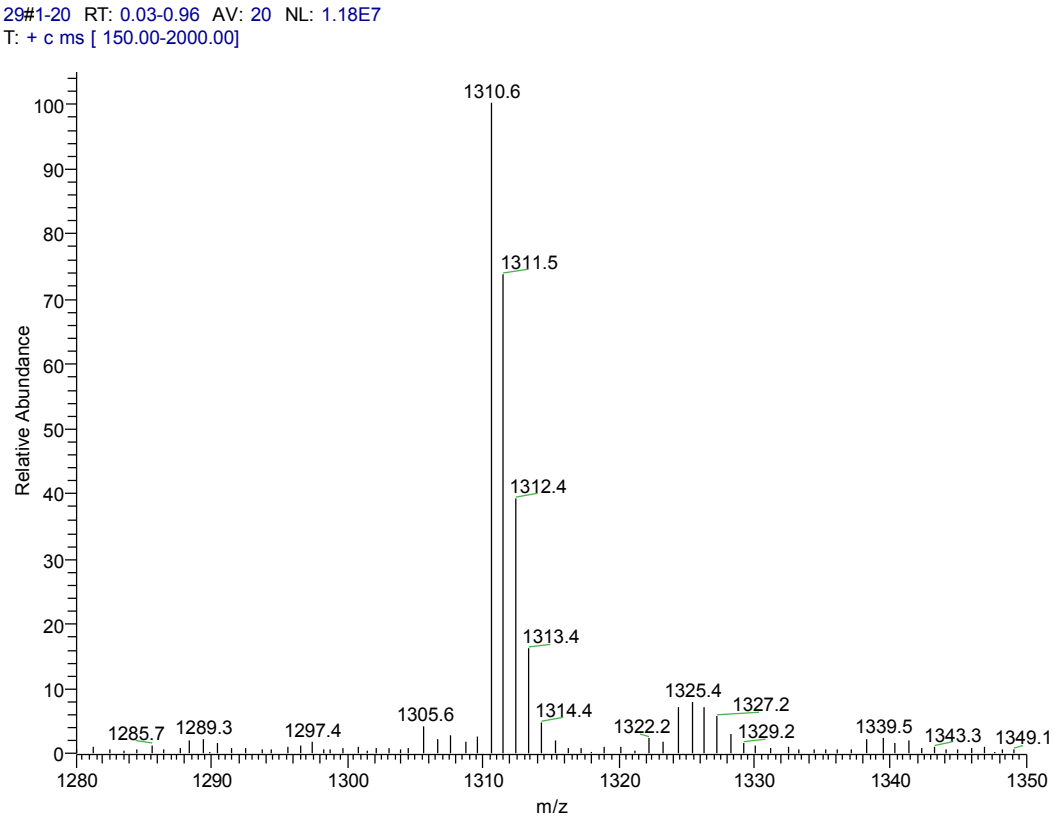

Fig. 10. ESI MS spectrum of the of the hexacyclic tetraacid (**2, 5-7**).

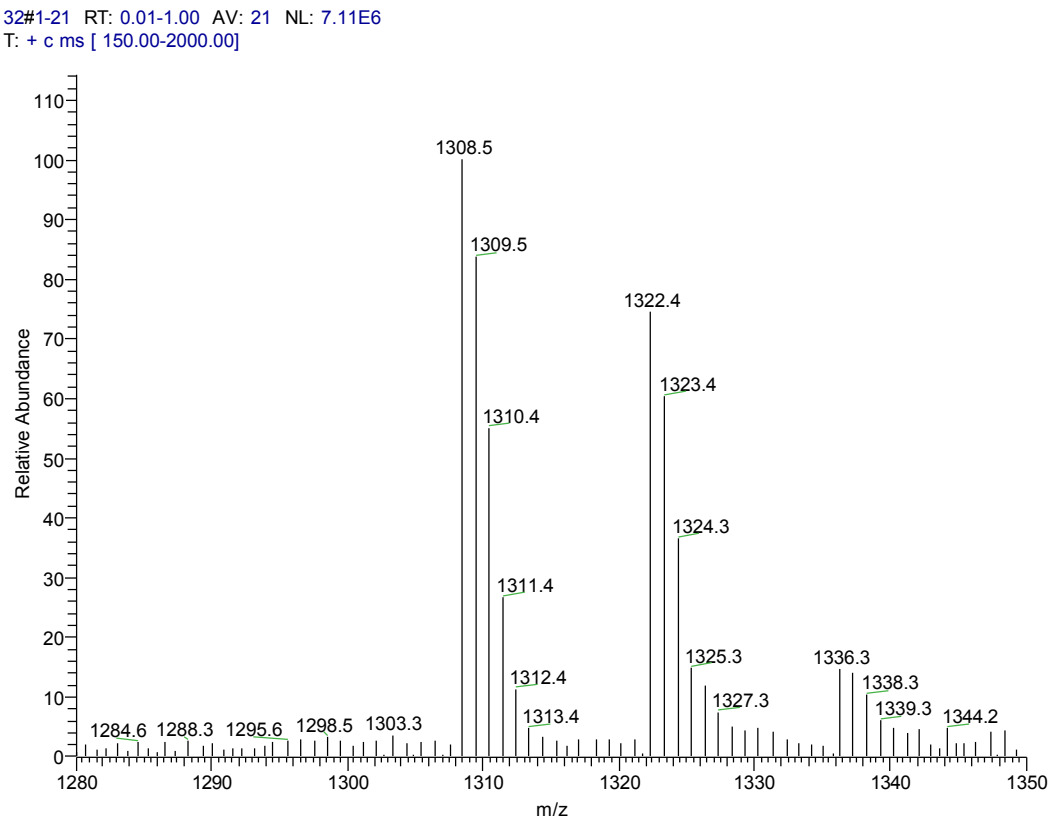

Fig. 11. ESI MS spectrum of the mixture of C_{80}, C_{81} and C_{82} heptacyclic tetraacids (structures not given).

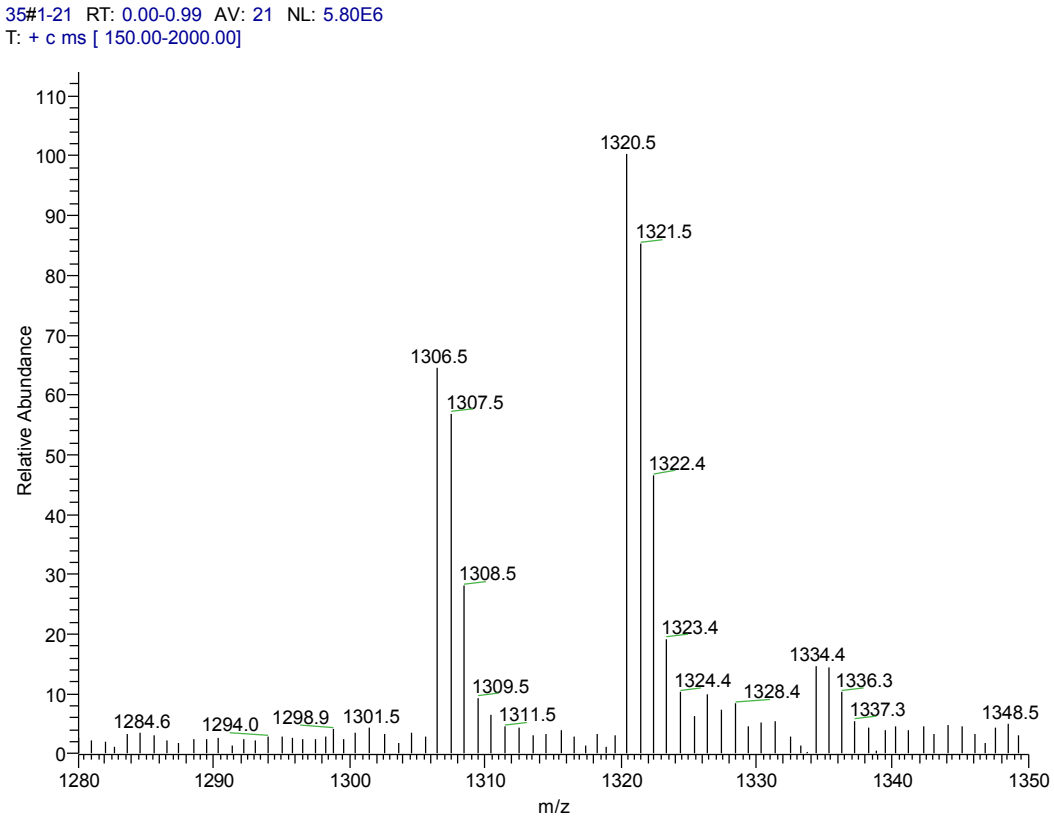

Fig. 12. ESI MS spectrum of the mixture of C_{80}, C_{81} and C_{82} octacyclic tetraacids (**4**, **8**, **9**).

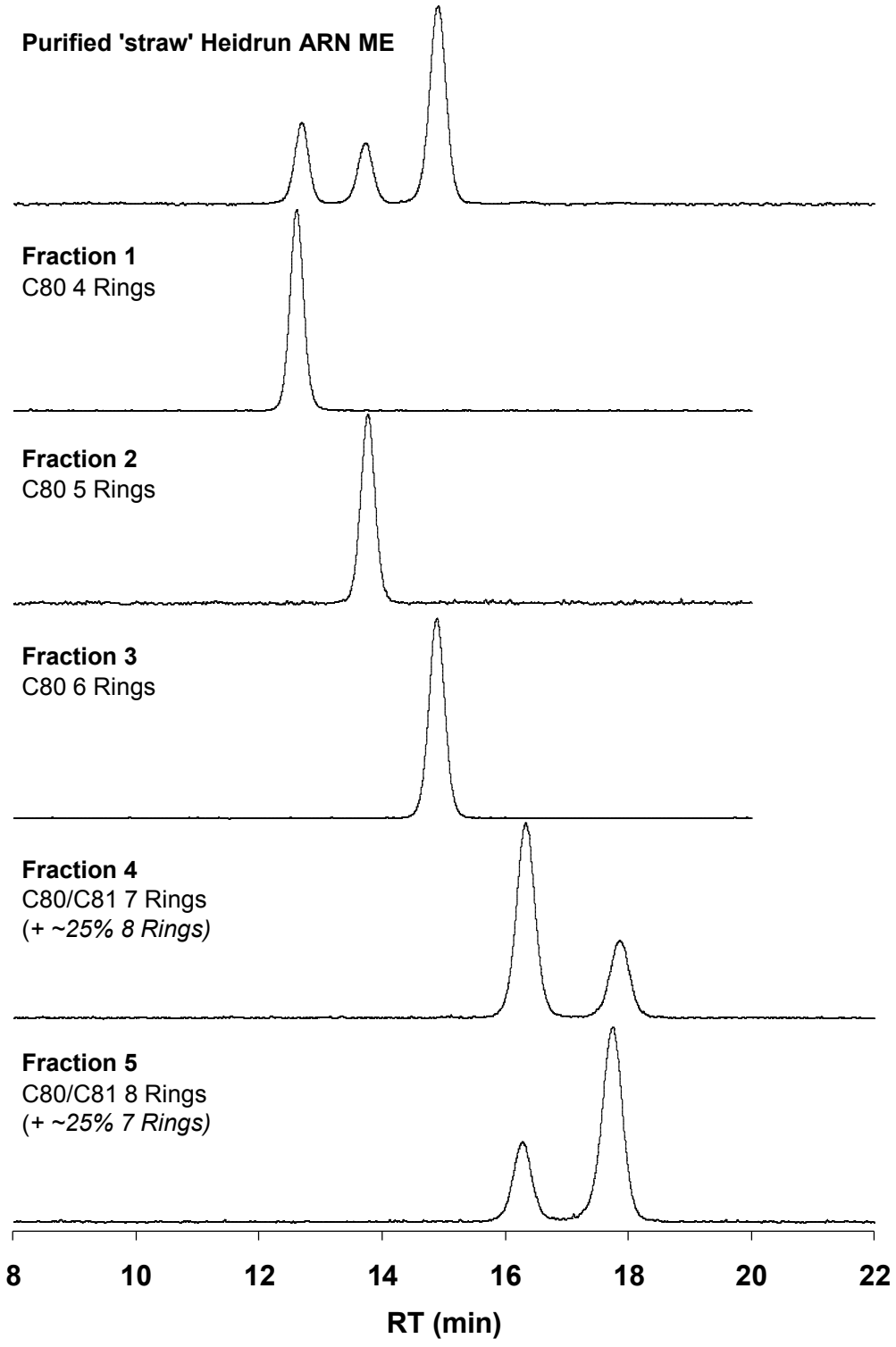

Fig. 13. HPLC-ELSD chromatograms of the mixture of tetraacids isolated from naphtenate deposits, and of the individual fractions analysed by NMR and MS spectroscopy. Expermental details are given in Ref 8.

Table 1 NMR data (800 MHz, $CDCl_3$, 298 K) for hexacyclic C_{80} isoprenoid tetraacid tetramethyl esters with 4 rings (**3**), 8 rings (**4**) and 6 rings (**2**, **5**-**7**), and for the 8-ring C_{82} analogue with extra methyl groups at C-13/C-13'.

Carbon #	Tetracyclic (**3**)		Octacyclic (**4**)		Hexacyclic (**2**, **5**-**7**)[a]			Octacyclic C_{82} (**9**)[b]	
	δ_C (ppm)	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)	δ_C (ppm)		δ_H (ppm)	δ_C (ppm)	δ_H (ppm)
1	173.85[c]		173.87[c]		173.9	173.9			
1'									
2	41.69	2.11/2.31	40.52	2.32	41.69	41.69	2.32/2.12		
2'					40.52	40.52	2.33		
3	30.36	1.95	36.41	2.23	30.36	30.36	1.95		
3'					36.41	36.41	2.23		
4	36.95	1.18/1.30	31.52	1.23/1.82	36.95	36.95	1.18/1.30		
4'					31.52	31.52	1.23/1.82		
5	25.867	1.26/1.30	30.34	1.25/1.75	25.873	25.867	1.26/1.31		
5'	25.871				30.33	30.33	1.25/1.75		
6	36.94	1.25/1,25	46.344	1.67	36.95	36.95	1.26/1.26		
6'			46.351		46.346	46.352	1.67		
7	39.00	1.79	45.511	1.63	39.01	39.01	1.80		
7'			45.517		45.512	45.518	1.63		
8	33.322	1.05/1.79	32.495	1.10/1.75	33.322	33.315	1.05/1.79		
8'	33.315		32.505		32.497	32.507	1.10/1.75		
9	31.274	1.12/1.75	31.43	1.10/1.74	31.283	31.276	1.12/1.75		
9'	31.281				31.43	31.43	1.10/1.74		
10	44.888	1.67	45.094	1.66	44.887	44.847	1.67	45.03	1.68
10'	44.847		45.127		45.093	45.127	1.66		
11	38.268	1.23	38.264	1.22	38.269	38.300	1.23	35.14	1.37
11'	38.298		38.300		38.300	38.264			
12	35.73	1.02/1.38	35.676	1.01/1.37	35.798	35.730	1.03/1.36 1.02/1.36	44.46	0.90/1.24
12'	35.80	1.03/1.36	35.738	1.02/1.36	35.674	35.739	1.01/1.37 1.02/1.36		
13	24.09	1.17/1.32	24.09	1.16/1.31	24.091	24.076	1.17/1.32	27.71	1.53
13'	24.42	1.15/1.38	24.41	1.14/1.37	24.414	24.421	1.15/1.37		
14	34.17	1.18/1.21	34.16	1.18/1.20	34.173	34.159	1.18/1.21	41.33	0.87/1.20
14'	37.52	1.06/1.28	37.51	1.06/1.28	37.517	37.526	1.03/1.28		
15	37.96	1.22	37.94	1.21	37.946	37.938	1.22	35.19	1.32
15'	33.21	1.34	33.19	1.34	33.194	33.202	1.34		
16	30.74	1.21/1.23	30.73	1.21/1.23	30.73	30.73	1.20/1.23		
16'	33.79	1.06/1.25	33.77	1.06/1.25	33.773	33.787	1.06/1.25		
17	19.72	0.94	39.13	0.77/1.96	19.72	19.72	0.94		
17'					39.120	39.128	0.78/1.96		
18	36.004	1.30/1.40	34.704	1.37/1.37	36.031	36.005	1.30/1.40		
18'	36.030		34.683		34.684	34.703	1.37/1.37		
19	17.754	0.84	17.723	0.84	17.748	17.755	0.84	17.85	0.83
19'	17.748		17.731		17.732	17.724			
20	30.16	1.19	30.16	1.19	30.15	30.15	1.19		
20'	19.89	0.86	19.89	0.86	19.89	19.89	0.86		
13-Me								21.33	0.84
OMe	51.35	3.673	51.36	3.667	51.346	51.363	3.67		

[a] Left ^{13}C column gives chemical shifts for the major set of signals due to cyclopentyl moiety close to bridge, as in **5**; right ^{13}C column gives chemical shifts for the minor set of signals due to bicyclopentyl moiety close to the bridge as in **2**.

[b] Only shift data for positions with significant changes in chemical shifts compared to **4** are given.

[c] Chemical shifts interchangeable.