Supporting Information

Chemical Characterization and Botanical Origin of French Ambers

Youssef A. Nohra, [*,†,‡,§] Vincent Perrichot, [*,†] Laurent Jeanneau,[†] Laurent Le Pollès,[⊥] and Dany Azar[§]

[†]CNRS UMR 6118 Géosciences and OSUR, Université de Rennes 1, Campus de Beaulieu bât. 15, 263 avenue du Général Leclerc, 35042 Rennes cedex, France

[‡]Doctoral School, PRASE Lebanese University, Campus Hadath-BP5, Beirut, Lebanon

[§]Department of Natural Sciences, Faculty of Sciences II, Lebanese University, Fanar-Matn, P.O. Box 26110217, Lebanon

[⊥]Institut des Sciences Chimiques de Rennes, CNRS UMR 6226, Ecole Nationale Supérieure de Chimie de Rennes, 11 allée de Beaulieu, 35708 Rennes cedex 7, France

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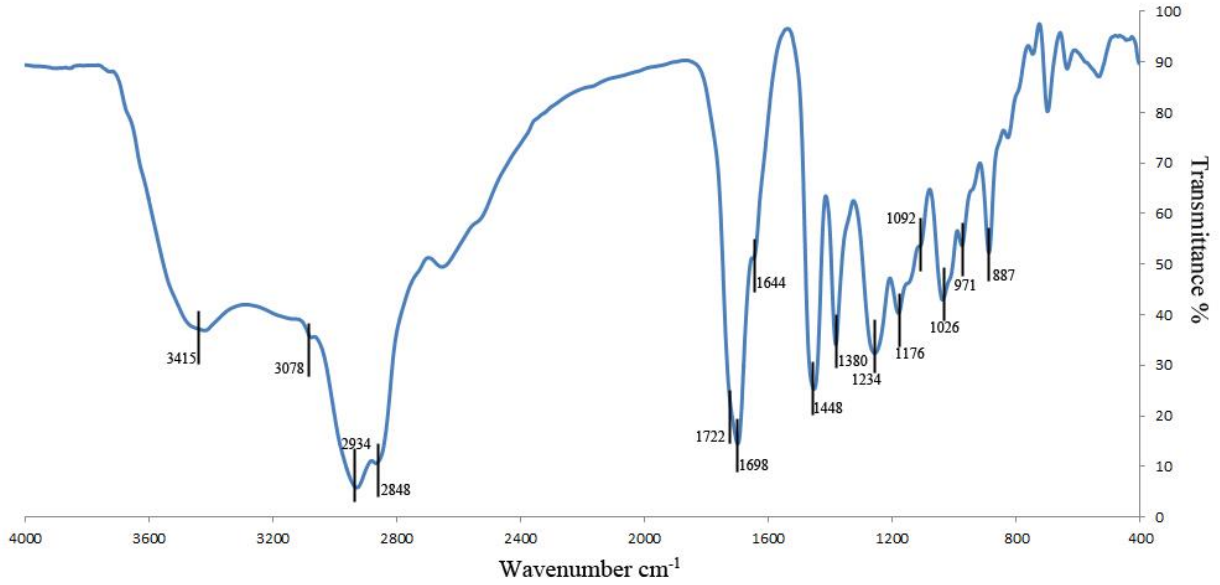

Figure S1. Infrared spectrum of Eocene Oise amber.

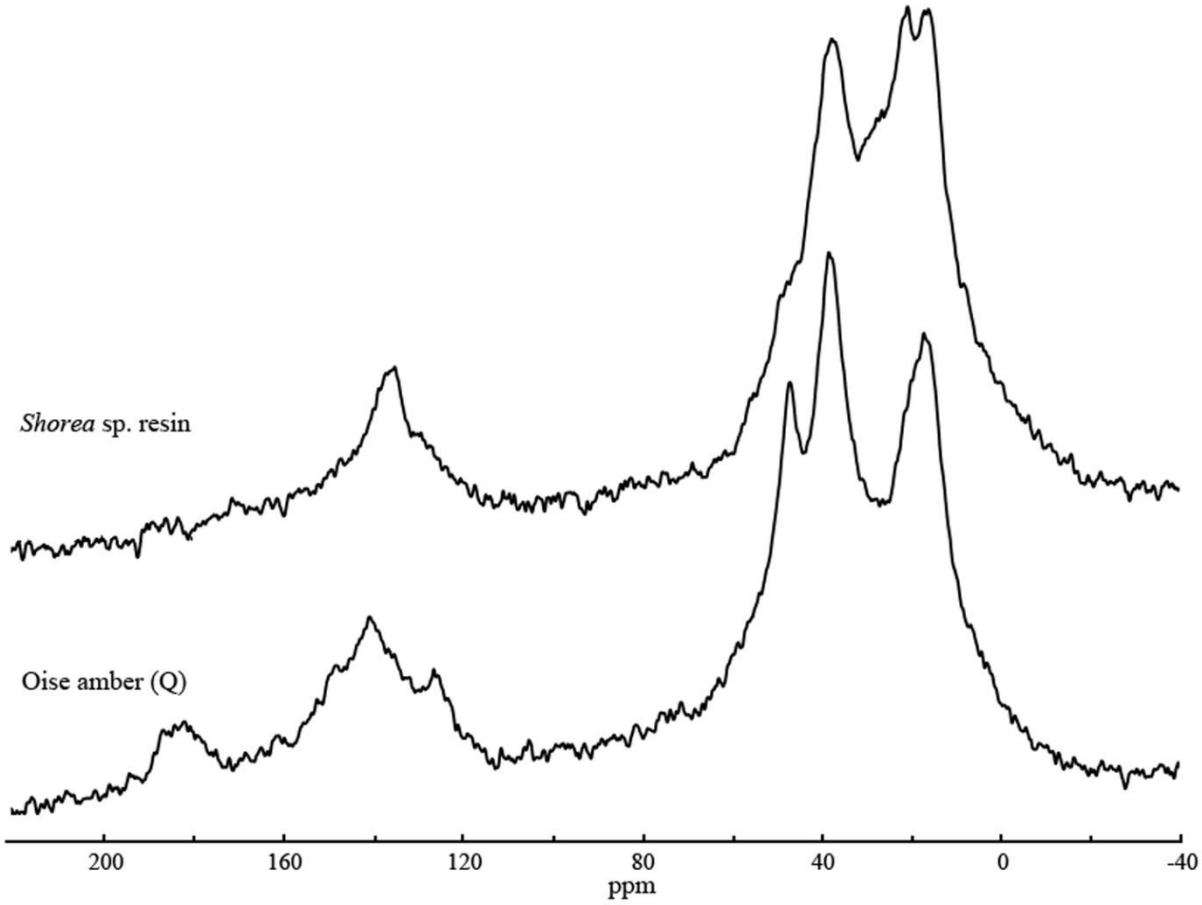

Figure S2. Solid State ^{13}C NMR spectra of *Shorea* sp. resin (above) and Eocene Oise amber (below).

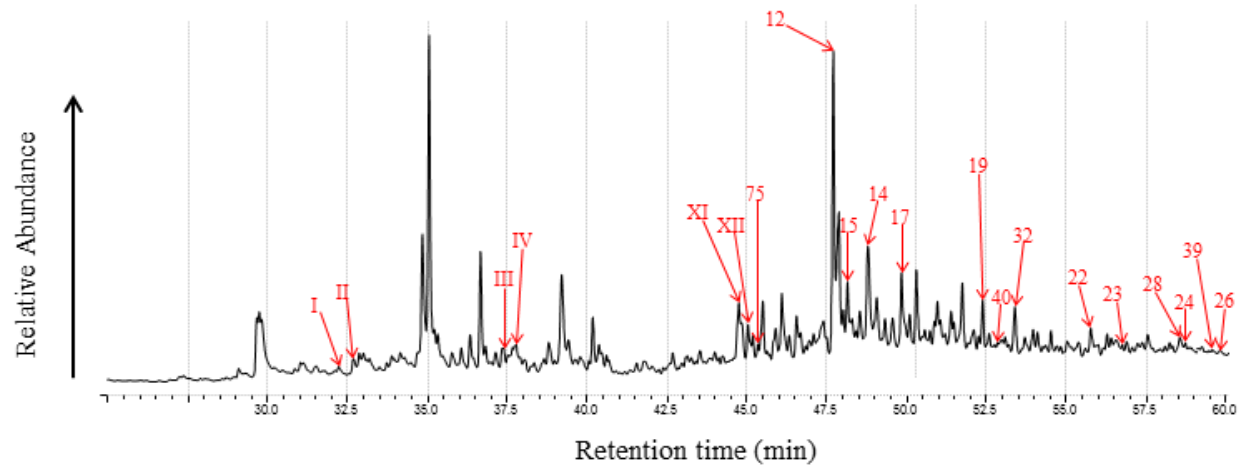

Figure S3. Thermochemolysis-GC-MS Total Ion Chromatogram (TIC) of Cenomanian Alpine amber from Salignac (numbered peaks refer to compounds in Table 1 and Table S1, Supporting information).

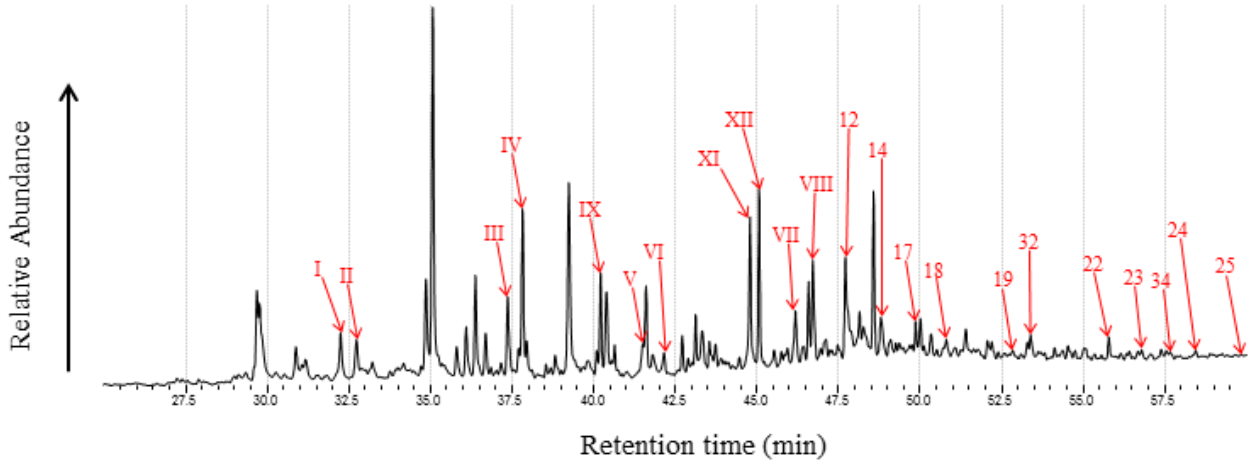

Figure S4. Thermochemolysis-GC-MS Total Ion Chromatogram (TIC) of Santonian Provence amber from Piolenc (numbered peaks refer to compounds in Table 1 and Table S1, Supporting information).

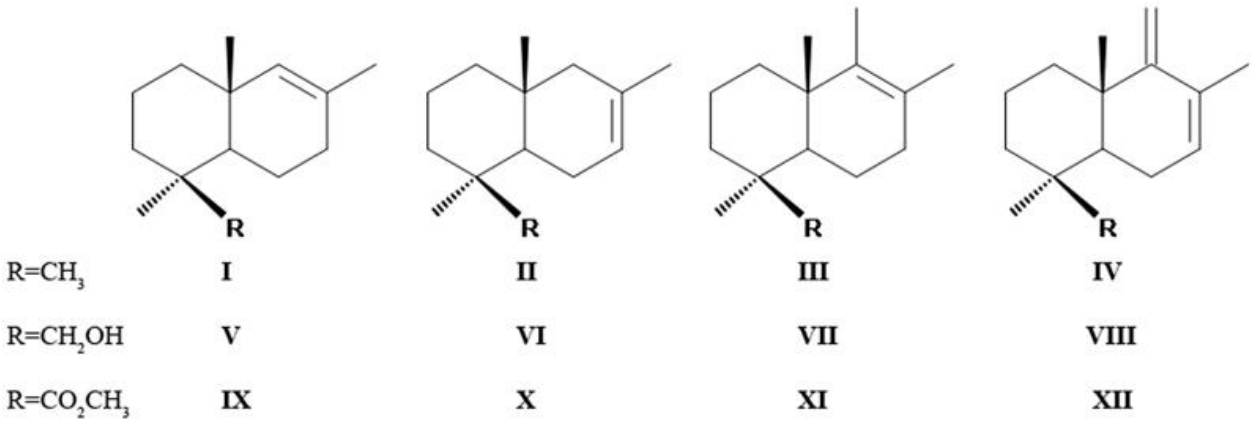

Figure S5. Structures of characteristic bicyclic products observed in the pyrolysates of Class Ib French Cretaceous ambers.

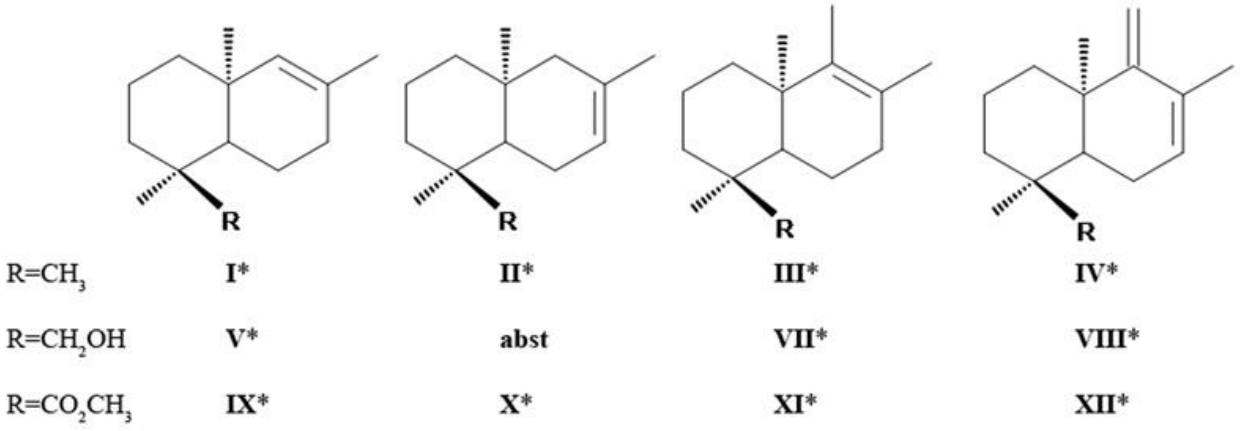

Figure S6. Structures of characteristic bicyclic products observed in the pyrolysates of Class Ic French Eocene Amber.

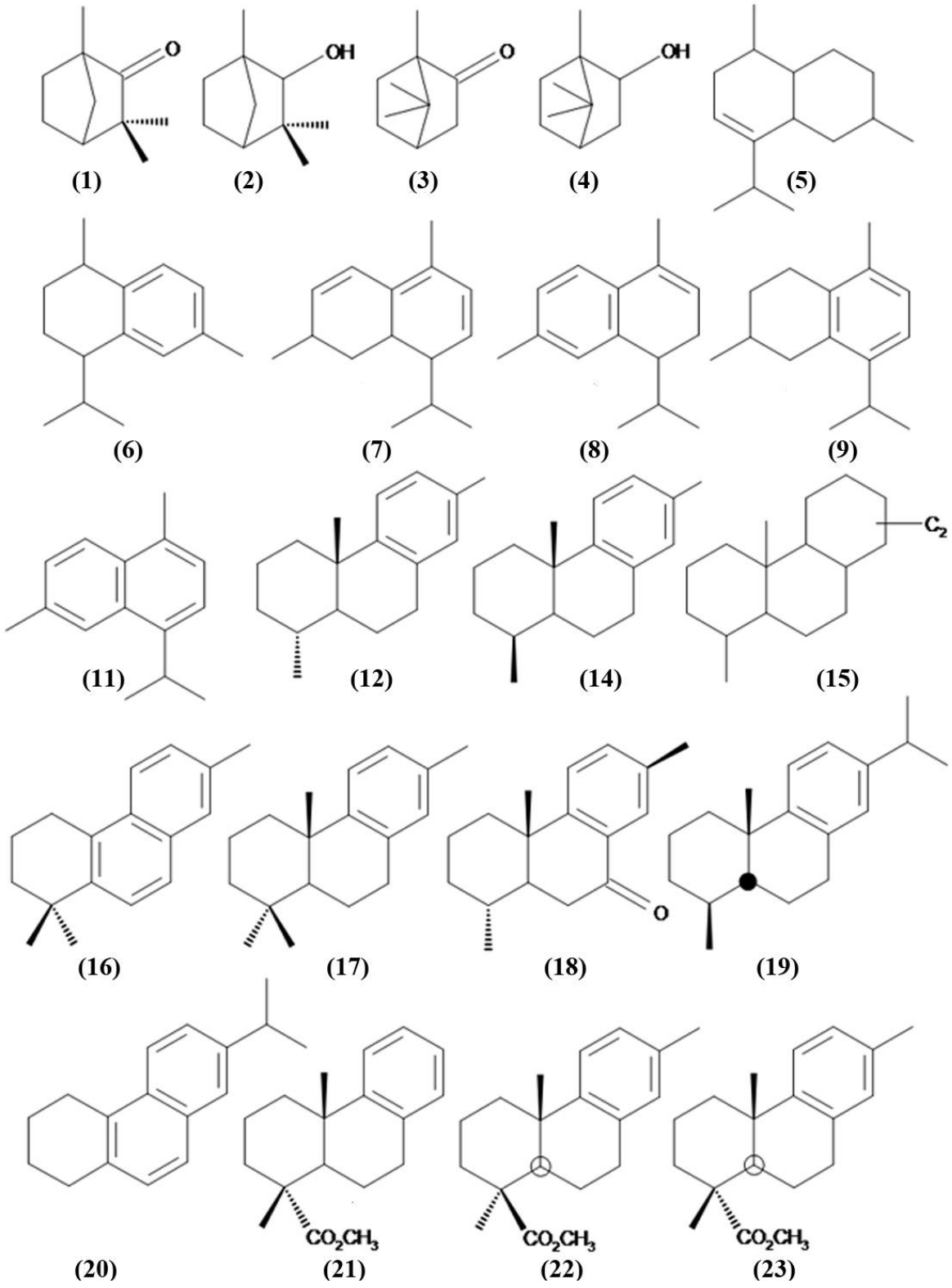

Figure S7. Structures of compounds **1-23**.

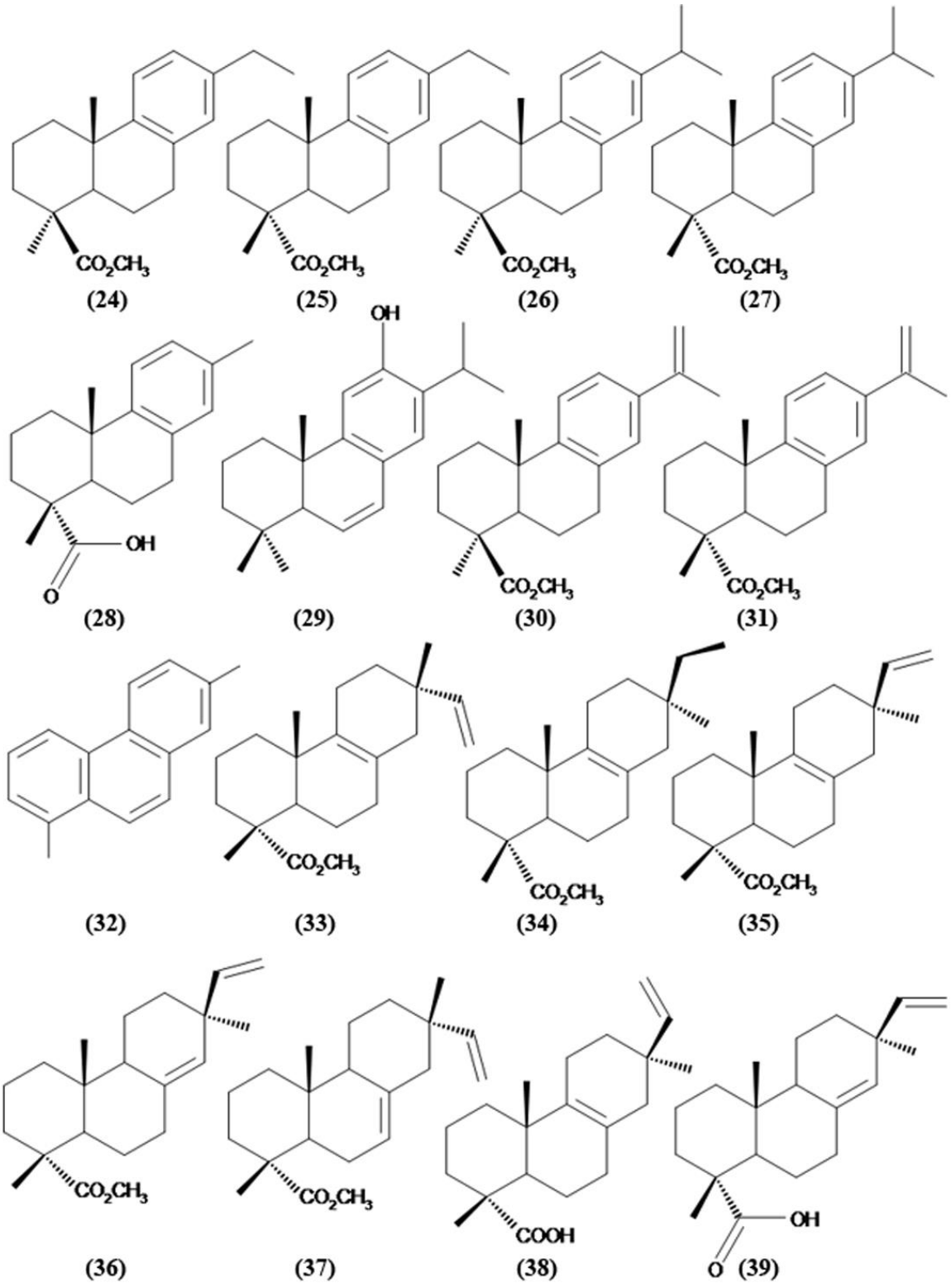

Figure S8. Structures of compounds **24-39**.

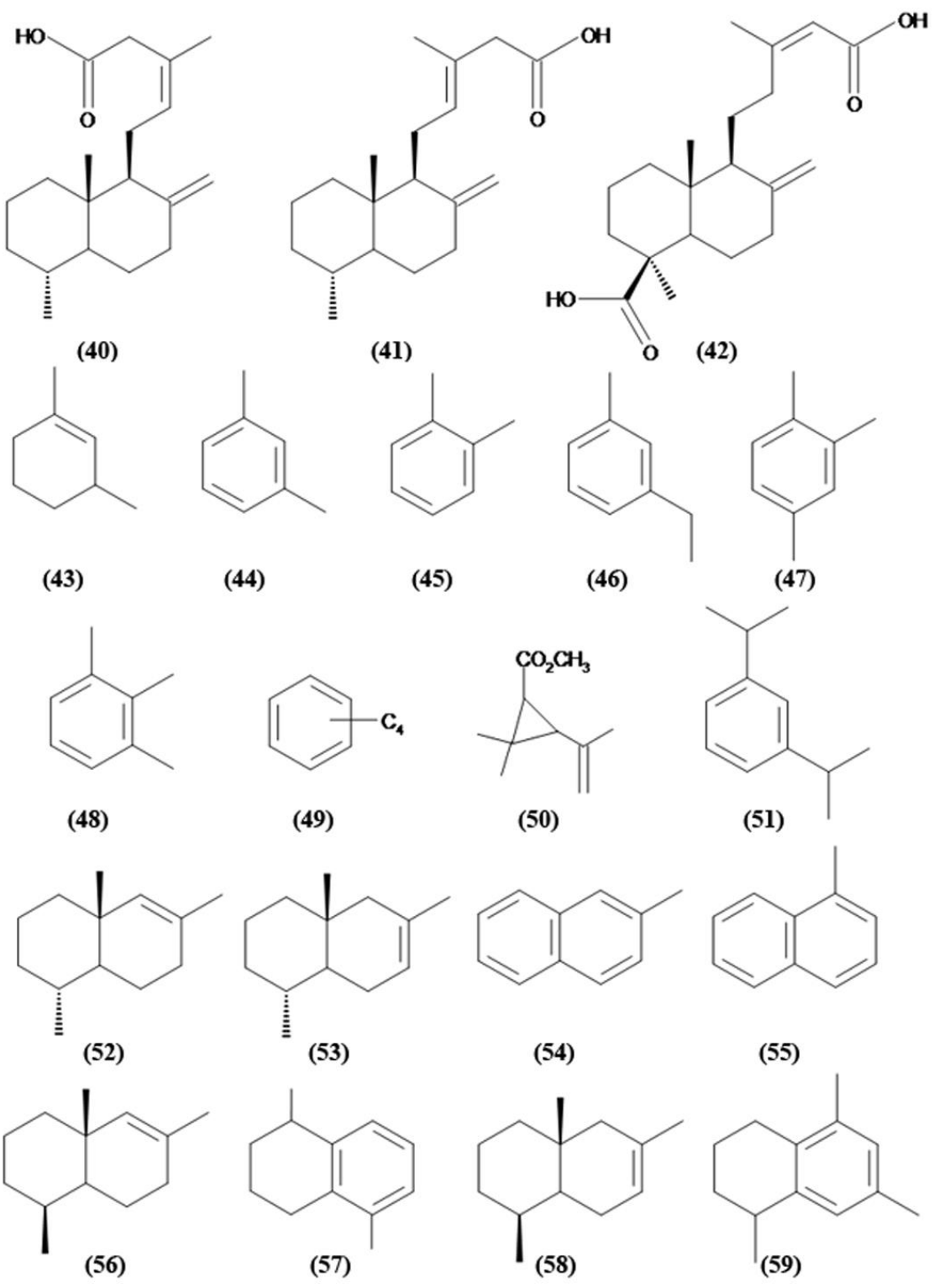

Figure S9. Structures of compounds **40-59**.

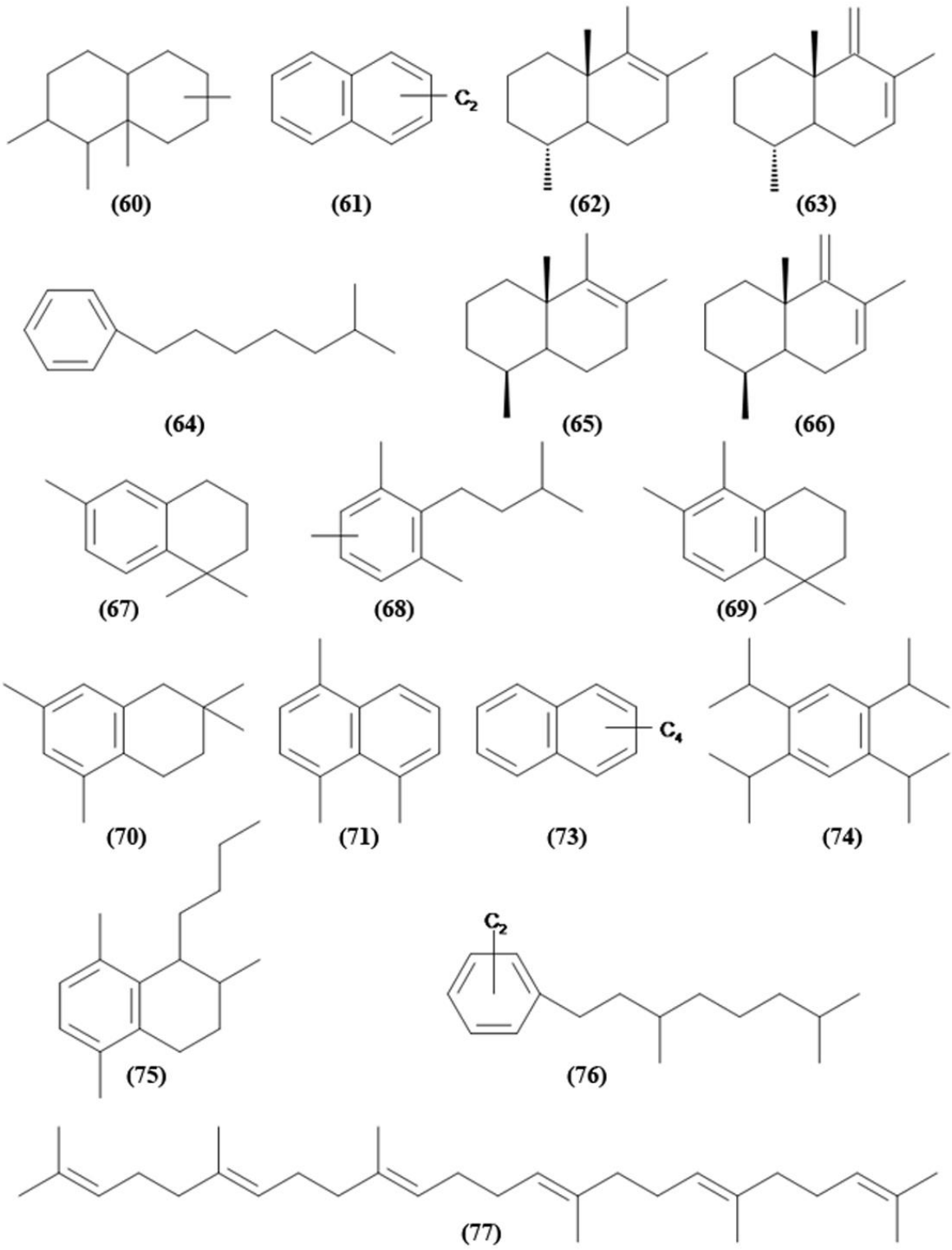

Figure S10. Structures of compounds **60-77**.

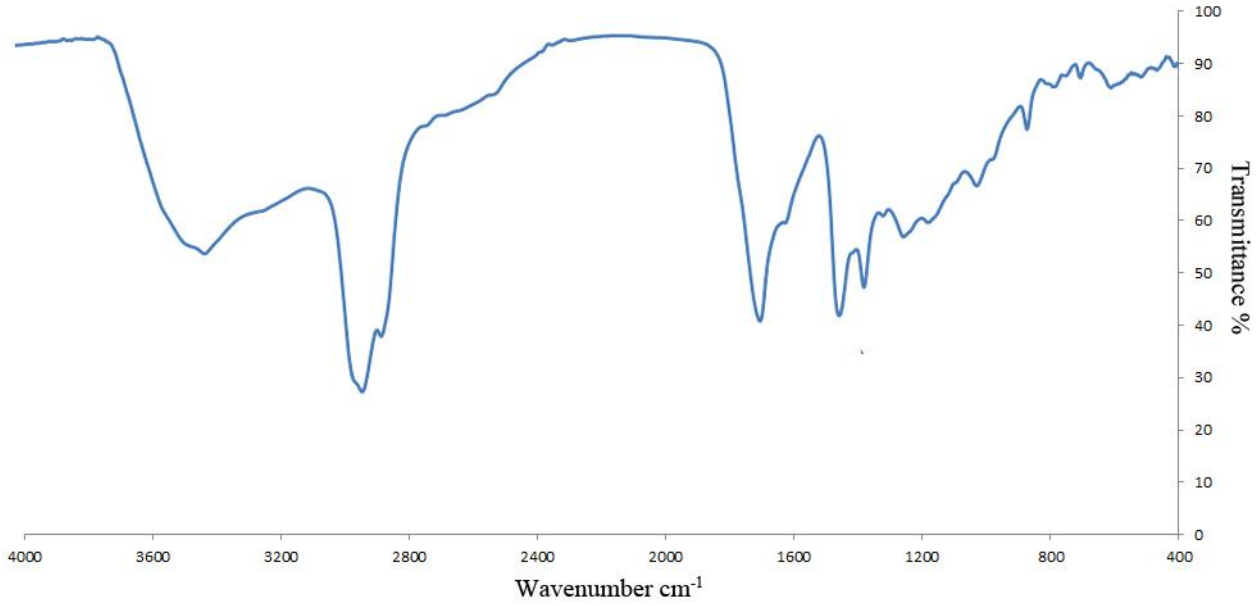

Figure S11. Infrared spectrum of Triassic Italian amber.

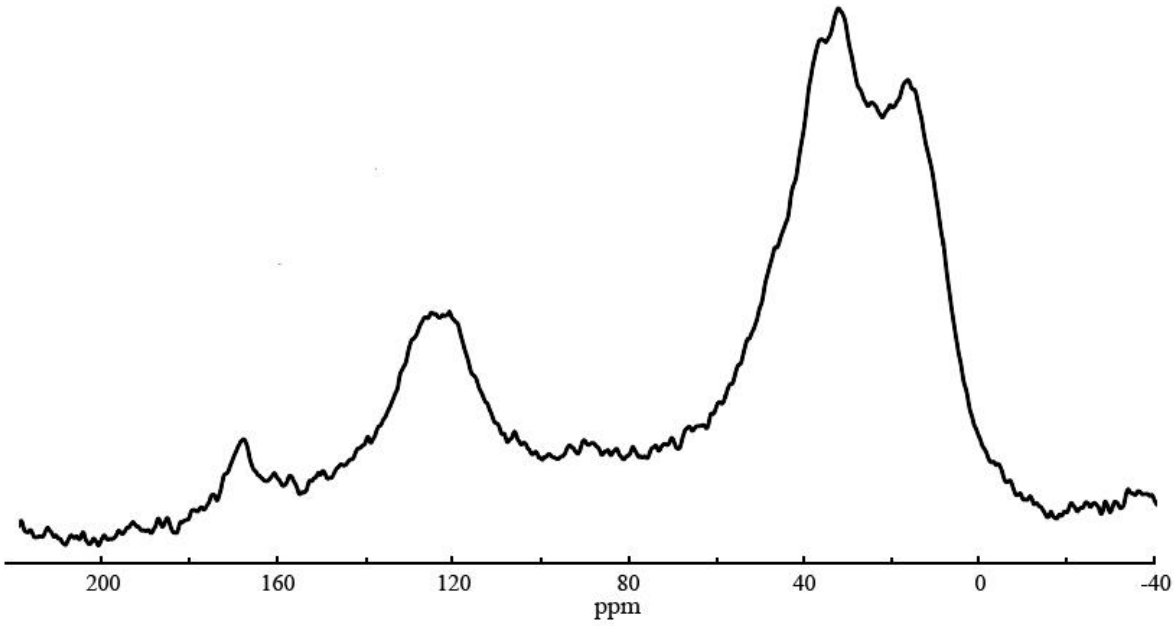

Figure S12. Solid State ^{13}C NMR spectrum of Triassic Italian amber.

Table S1. List of the Studied Samples with Details on their Age and the Possible Resin Sources Found Associated with the Amber. (* In Same Geological Level from Neighboring Outcrops).

sample	locality	age	possible resin-source (from independent botanical remains)
A1, A2	Archingeay	Late Albian[S1]	Cheirolepidiaceae: *Agathoxylon*, *Frenelopsis*, *Classopollis* Cupressaceae: *Glenrosa* Podocarpaceae: *Podocarpoxylon* *Protopodocarpoxylon* [S9, S10]
F1, F2	Fouras	Early Cenomanian[S2]	
S	Salignac	Cenomanian [S3]	No data
Fo	Fourtou	Middle Cenomanian [S4]	Cheirolepidiaceae: *Agathoxylon*, *Frenelopsis* Cupressaceae: *Glenrosa* [S4]
D	Durtal	Early Cenomanian [S5]	*Protopodocarpoxylon* Araucariaceae* Cheirolepidiaceae*: *Frenelopsis*, *Geinitzia*, *Classopollis* Cupressaceae* [S11]
G	La Garnache	Early Santonian [S6]	Pinaceae Taxodiaceae (Cupressaceae s.l.) (pers. data)
P	Piolenc	Early Santonian [S7]	Araucariaceae: *Pagiophyllum* [S12]
B	Belcodène	Early Santonian [S3]	No data
Q	Le Quesnoy	Earle Eocene [S8]	Fabaceae: *Aulacoxylon* [S13]

Table S2. Compounds Identified in the French Cretaceous Ambers.

No	compound name	BP	MW	occurrence in sample									
				A1	A2	F1	F2	S	Fo	D	G	P	B
monoterpenoids													
1	fenchone	81	152	-	0.27	-	-	-	-	-	-	-	-
2	fenchol	95	154	-	0.07	-	-	-	-	-	-	-	-
3	camphor	81	152	-	0.45	-	-	-	-	-	-	-	-
4	borneol	95	154	-	0.40	-	-	-	-	-	-	-	-
sesquiterpenoids													
5	dihydrocadinene	109	206	-	0.49	-	-	-	-	-	-	-	-
6	calamenene	159	202	0.62	0.11	0.40	0.13	0.23	0.33	0.27	0.20	0.33	0.16
7	cadala-1(10),3,8-triene	157	202	0.34	0.75	0.41	1.02	-	0.98	-	-	-	-
8	α-calacorene	157	200	-	-	-	-	0.57	-	0.29	0.74	0.65	1.21
9	5,6,7,8-tetrahydrocadalene	187	202	0.97	2.04	1.06	1.30	2.12	2.11	1.69	6.61	8.26	3.98
10	calamanene isomer	159	202	0.14	0.34	0.11	0.27	-	1.11	1.01	-	-	-
11	cadalene	183	198	-	0.30	-	0.27	-	0.22	-	0.29	0.26	0.28
diterpenoids													
abietanes and podocarpanes													
12	16,17,19-trisnorabieta-8,11,13-triene	131	228	2.67	4.17	1.80	3.07	15.94	4.61	3.55	4.88	3.67	3.10
13	bisnorabietane isomer	109	248	-	0.14	-	-	-	-	0.68	-	-	-
14	16,17,18-trisnorabieta-8,11,13-triene	131	228	2.40	2.51	1.29	2.03	1.67	1.93	1.41	2.57	1.15	1.08
15	bisnorabietane	109	248	-	0.18	-	-	0.65	0.05	0.33	-	-	-
16	16,17-bisnorsimonellite	209	224	0.29	0.94	0.30	1.36	-	0.52	-	-	-	-
17	16,17-bisnordehydroabietane	227	242	0.84	0.79	0.25	0.94	1.25	0.31	0.53	1.21	0.50	0.67
18	7-oxo-16,17,18-trisnorabieta-8,11,13-triene	145	242	-	0.27	0.15	0.08	0.70	0.50	0.59	1.09	0.74	0.63
19	dehydroabietin	159	256	-	-	-	-	0.60	0.09	-	-	0.12	-
20	bisnorsimonellite	209	224	0.46	0.71	0.11	0.59	-	0.13	-	-	-	-
21	methyl-15,16,17-trinordehydroabietate	197	272	0.58	0.19	0.10	0.64	-	-	0.93	-	-	-
22	methyl-16,17-dinorcallitrisate	211	286	2.28	2.08	0.76	1.94	0.55	0.28	3.76	2.09	0.79	3.18
23	methyl-16,17-dinordehydroabietate	211	286	3.66	4.56	1.53	5.02	0.30	0.50	9.21	0.64	0.53	1.52
24	methyl-17-norcallitrisate	225	300	0.43	0.41	0.06	0.52	0.14	0.26	0.72	0.45	0.27	0.93
25	methyl-17-nordehydroabietate	225	300	0.27	0.11	0.04	0.15	-	-	0.19	0.09	0.04	0.38
26	methyl callitrisate	239	314	0.23	0.10	0.07	0.36	0.04	-	0.28	0.03	-	0.22
27	methyl dehydroabietate	239	314	-	-	-	0.04	-	-	-	-	-	0.20
28	16,17-bisnordehyroabietic acid	211	272	-	-	-	-	0.37	0.22	-	-	-	-
29	12-hydroxysimonellite	253	268	-	-	-	-	-	0.27	-	-	-	-
30	methyl-15,16-dehydrocallitrisate	237	312	-	-	-	-	-	-	0.08	-	-	-
31	methyl Abieta-8,11,13,15-tetraen-18-oate	237	312	-	-	-	-	-	-	0.09	-	0.02	0.12

[a] All Compound Structures are Presented in Figures S10–S13. (BP: base peak; MW: Molecular Weight; 28, 38, 39 Analyzed as TMS Derivatives; 40–42 Analyzed as Methylated Derivatives).

Table S2. (Continued)

No	compound name	BP	MW	occurrence in sample									
				A1	A2	F1	F2	S	Fo	D	G	P	B
pimaranes and isopimaranes													
32	pimanthrene	206	206	3.23	8.05	1.67	7.83	2.06	2.93	2.49	2.91	0.97	1.09
33	methyl 8,15-isopimaradien-18-oate	241	316	0.36	0.71	0.19	1.41	-	-	0.83	-	-	-
34	methyl-8-pimaren-18-oate	243	318	1.92	1.72	0.63	1.71	0.05	0.03	1.77	0.21	0.12	0.22
35	methyl-8,15-pimaradiene-18-oate	241	316	0.17	0.12	0.03	0.43	-	-	0.40	-	-	-
36	methyl pimarate	121	316	0.18	0.57	0.06	0.33	-	-	1.94	-	-	-
37	methyl isopimarate	241	316	0.16	0.19	0.02	0.21	-	-	0.10	-	-	-
38	pimara-8,15-dien-18-oic acid	241	374	0.03	0.08	-	0.12	-	-	-	-	-	-
39	pimaric acid	73	374	-	-	-	-	0.11	-	-	-	-	-
labdanes													
40	Z-19-noragathic acid	215	304	0.16	-	-	-	0.18	-	-	-	-	-
41	E-19-noragathic acid	215	304	0.09	-	0.02	-	-	0.18	-	-	-	-
42	agathic acid	121	362	0.08	0.11	-	-	-	-	-	-	-	-
other compounds													
43	1,3-dimethyl-1-cyclohexene	95	110	1.13	1.17	4.05	1.21	4.92	2.32	1.24	2.98	6.44	0.82
44	1,3-dimethylbenzene	91	106	0.81	1.49	3.60	1.21	-	1.46	-	1.23	-	-
45	1,2-dimethylbenzene	91	106	1.00	0.22	1.39	-	1.04	0.71	-	0.33	-	-
46	1-methyl-3-ethylbenzene	105	120	1.02	0.30	1.48	0.45	0.72	0.80	0.82	-	-	-
47	1,2,4-trimethylbenzene	105	120	1.10	0.25	1.97	0.82	0.55	5.63	2.35	-	-	-
48	1,2,3-trimethylbenzene	105	120	2.44	0.31	3.26	1.82	2.84	0.82	1.54	1.54	1.71	2.84
49	tetramethylbenzene	119	134	0.03	0.30	0.40	-	0.56	1.10	-	-	-	0.21
50	norchrysamthemic acid methyl ester	109	168	1.57	1.35	2.94	2.63	0.85	0.27	4.95	2.00	2.13	7.65
51	1,3-bis(1-methyl ethyl) benzene	147	162	0.15	0.21	0.10	0.31	-	-	-	-	-	-
52	naphthalene-1,2,3,4,4a,7,8,8a-octahydro-1,4a,6-trimethyl [1R, 4aS, 8aS]	81	178	0.94	2.87	1.50	1.98	3.28	2.46	1.62	6.58	6.31	2.53
53	naphthalene-1,2,3,4,4a,5,8,8a-octahydro-1,4a,6-trimethyl [1R, 4aR, 8aS]	95	178	0.88	1.06	1.10	0.91	2.84	1.73	1.08	2.98	1.71	1.30
54	2-methylnaphthalene	142	142	-	0.05	-	-	-	-	-	-	-	-
55	1-methylnaphthalene	142	142	-	0.05	-	-	-	-	-	-	-	-
56	naphthalene-l,2,3,4,4a,7,8,8a-octahydro-1,4a,6-trimethyl [1S, 4aS, 8aS]	95	178	0.37	0.80	0.65	0.52	0.14	0.39	0.58	1.31	1.47	0.61
57	1,2,3,4-tetrahydro-1,5-dimethylnaphthalene	145	160	0.62	0.92	1.57	1.16	1.29	2.20	1.47	1.85	1.29	1.33
58	naphthalene-l,2,3,4,4a,5,8,8a-octahydro-l,4a,6-trimethyl[lR, 4aR, 8aS]	95	178	0.09	0.50	0.38	0.32	0.31	-	0.64	0.70	0.44	0.22
59	1,5,7-trimethyl-1,2,3,4-tetrahydronaphthalene	159	174	0.57	0.29	0.77	0.56	0.42	0.37	0.37	0.74	0.73	0.75
60	tetramethyl decalin	109	194	0.20	0.48	0.09	0.39	1.02	0.68	0.34	-	-	-
61	dimethyl naphthalene	156	156	0.70	0.90	0.89	1.33	0.52	0.84	0.68	1.17	0.43	1.08
62	naphthalene-l,2,3,4,4a,7,8,8a-octahydro-1,4a,5,6-tetramethyl [lR, 4aS, 8aS]	95	192	4.17	9.80	4.89	6.29	11.98	8.41	6.48	7.79	9.28	5.25
63	naphthalene-l,2,3,4,4a,5,8,8a-octahydro-5-methylene-1,4a,6-trimethylI [lR, 4aS, 8aS]	108	190	2.75	6.40	5.78	4.26	9.89	5.65	3.85	6.09	11.48	3.57
64	6-methylheptylbenzene	147	190	0.10	0.47	0.52	0.69	2.61	2.90	0.36	-	-	2.22
65	naphthalene-1,2,3,4,4a,7,8,8a-octahydro-1,4a,5,6-tetramethyl [1S, 4aS, 8aS]	95	192	2.14	3.48	2.99	2.55	1.07	1.46	2.02	1.87	2.65	1.03
66	naphthalene-1,2,3,4,4a,5,8,8a-octahydro-5-methylene-1,4a,6trimethyl [lS, 4aS, 8aS]	93	190	0.88	2.65	2.21	1.36	0.85	0.96	1.28	1.53	2.55	0.78
67	ionene	159	174	3.52	4.98	4.89	3.86	11.54	13.11	3.11	4.43	4.70	10.00
68	trimethylisopentylbenzene	133	190	-	0.04	0.01	0.03	1.10	1.20	0.23	0.12	0.24	0.64
69	methylionene	173	188	1.37	1.60	1.42	1.74	1.40	3.39	1.41	1.85	2.35	3.45

Table S2. (Continued)

No	compound name	BP	MW	occurrence in sample									
				A1	A2	F1	F2	S	Fo	D	G	P	B
70	1,2,3,4,-tetrahydro-2,2,5,7-tetramethylnaphthalene	133	188	-	-	-	-	0.49	0.81	-	-	-	-
71	1,4,5-trimethylnaphthalene	155	170	-	-	-	-	3.53	7.30	-	-	-	-
72	methylionene isomer	173	188	0.94	0.15	1.96	0.31	0.91	1.17	0.20	0.18	0.23	0.08
73	tetramethyl naphthalene	169	184	0.78	1.09	0.88	0.98	0.90	3.05	0.83	1.73	1.42	2.19
74	1,2,4,5-tetraisopropylbenzene	231	246	0.36	0.16	0.15	0.14	0.50	0.30	0.29	-	-	-
75	2,5,8-trimethyl-1-butyltetralin	159	230	0.75	-	0.17	-	0.74	0.67	-	-	-	-
76	3,7-dimethyloctylxylene	119	246	-	-	-	-	0.10	0.49	-	-	-	-
77	squalene	69	410	3.44	0.50	0.18	0.62	-	0.45	0.62	-	-	-

Table S3. Compounds Identified in the Italian Triassic Amber.

No	compound name	BP	MW	occurrence in sample
monoterpenoids				
1	fenchone	81	152	-
2	fenchol	95	154	-
3	camphor	81	152	0.119
4	borneol	95	154	-
Sesquiterpenoids				
5	dihydrocadinene	109	206	0.148
6	calamenene	159	202	1.289
7	cadala-1(10),3,8-triene	157	202	0.884
8	α-calacorene	157	200	-
9	5,6,7,8-tetrahydrocadalene	187	202	7.843
10	calamanene isomer	159	202	6.948
11	cadalene	183	198	0.532
diterpenoids				
abietanes and podocarpanes				
12	16,17,19-trisnorabieta-8,11,13-triene	131	228	3.931
13	bisnorabietane isomer	109	248	-
14	16,17,18-trisnorabieta-8,11,13-triene	131	228	0.479
15	bisnorabietane	109	248	-
16	16,17-bisnorsimonellite	209	224	0.411
17	16,17-bisnordehydroabietane	227	242	0.420
18	7-oxo-16,17,18-trisnorabieta-8,11,13-triene	145	242	2.069
19	dehydroabietin	159	256	0.207
20	bisnorsimonellite	209	224	0.620
21	methyl-15,16,17-trinordehydroabietate	197	272	0.238
22	methyl-16,17-dinorcallitrisate	211	286	3.212
23	methyl-16,17-dinordehydroabietate	211	286	0.089
24	methyl-17-norcallitrisate	225	300	0.028
25	methyl-17-nordehydroabietate	225	300	0.120
26	methyl callitrisate	239	314	0.098
27	methyl dehydroabietate	239	314	0.529
28	16,17-bisnordehyroabietic acid	211	272	-
29	12-hydroxysimonellite	253	268	-
30	methyl-15,16-dehydrocallitrisate	237	312	0.129
31	methyl Abieta-8,11,13,15-tetraen-18-oate	237	312	0.021
pimaranes and isopimaranes				
32	pimanthrene	206	206	2.385
33	methyl 8,15-isopimaradien-18-oate	241	316	-
34	methyl-8-pimaren-18-oate	243	318	0.028
35	methyl-8,15-pimaradiene-18-oate	241	316	-
36	methyl pimarate	121	316	0.120
37	methyl isopimarate	241	316	-
38	pimara-8,15-dien-18-oic acid	241	374	-
39	pimaric acid	73	374	-
labdanes				
40	Z-19-noragathic acid	215	304	-
41	E-19-noragathic acid	215	304	-
42	agathic acid	121	362	-

[a] Compound Structures are Presented in Figures S10–S13. (BP: base peak; MW: Molecular Weight; 28, 38, 39 Analyzed as TMS Derivatives; 40–42 Analyzed as Methylated Derivatives).

Table S3. (Continued)

No	compound name	BP	MW	occurrence in sample
other compounds				
43	1,3-dimethyl-1-cyclohexene	95	110	0.928
44	1,3-dimethylbenzene	91	106	3.600
45	1,2-dimethylbenzene	91	106	2.369
46	1-methyl-3-ethylbenzene	105	120	0.250
47	1,2,4-trimethylbenzene	105	120	1.526
48	1,2,3-trimethylbenzene	105	120	1.785
49	tetramethylbenzene	119	134	0.329
50	norchrysamthemic acid methyl ester	109	168	0.119
51	1,3-bis(1-methyl ethyl) benzene	147	162	1.325
52	naphthalene-1,2,3,4,4a,7,8,8a-octahydro-1,4a,6-trimethyl [1R, 4aS, 8aS]	81	178	0.093
53	naphthalene-1,2,3,4,4a,5,8,8a-octahydro-1,4a,6-trimethyl [1R, 4aR, 8aS]	95	178	2.669
54	2-methylnaphthalene	142	142	1.355
55	1-methylnaphthalene	142	142	1.563
56	naphthalene-l,2,3,4,4a,7,8,8a-octahydro-1,4a,6-trimethyl [1S, 4aS, 8aS]	95	178	0.060
57	1,2,3,4-tetrahydro-1,5-dimethylnaphthalene	145	160	0.019
58	naphthalene-l,2,3,4,4a,5,8,8a-octahydro-l,4a,6-trimethyl[lR, 4aR, 8aS]	95	178	0.327
59	1,5,7-trimethyl-1,2,3,4-tetrahydronaphthalene	159	174	1.915
60	tetramethyl decalin	109	194	0.229
61	dimethyl naphthalene	156	156	0.012
62	naphthalene-l,2,3,4,4a,7,8,8a-octahydro-1,4a,5,6-tetramethyl [lR, 4aS, 8aS]	95	192	0.089
63	naphthalene-l,2,3,4,4a,5,8,8a-octahydro-5-methylene-1,4a,6-trimethylI [lR, 4aS, 8aS]	108	190	0.126
64	6-methylheptylbenzene	147	190	1.296
65	naphthalene-1,2,3,4,4a,7,8,8a-octahydro-1,4a,5,6-tetramethyl [1S, 4aS, 8aS]	95	192	1.234
66	naphthalene-1,2,3,4,4a,5,8,8a-octahydro-5-methylene-1,4a,6trimethyl [lS, 4aS, 8aS]	93	190	3.907
67	ionene	159	174	4.386
68	trimethylisopentylbenzene	133	190	2.779
69	methylionene	173	188	0.258
70	1,2,3,4,-tetrahydro-2,2,5,7-tetramethylnaphthalene	133	188	-
71	1,4,5-trimethylnaphthalene	155	170	6.948
72	methylionene isomer	173	188	0.532
73	tetramethyl naphthalene	169	184	0.502
74	1,2,4,5-tetraisopropylbenzene	231	246	-
75	2,5,8-trimethyl-1-butyltetralin	159	230	-
76	3,7-dimethyloctylxylene	119	246	-
77	squalene	69	410	1.243

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