

Supplementary Material

Table S1. Simple correlation between the main constituents of the essential oils from leaves of *Piper gaudichaudianum* Kunth collected for seasonality study.

Compound	α -Cadinol	Bicyclogermacrene	<i>E</i> -Nerolidol	<i>E</i> -Caryophyllene	Eudesmadiene	Non-oxygenated Monoterpene	Oxygenated monoterpenes	Non-oxygenated Sesquiterpenes	Oxygenated sesquiterpenes
Bicyclogermacrene	-0.269								
(<i>E</i>)-Nerolidol	-0.508	-0.192							
<i>E</i> -Caryophyllene	0.294	0.340	-0.454						
Eudesmadiene	0.396	0.125	-0.746*	0.635*					
Non-oxygenated Monoterpene	-0.536	-0.057	0.457	-0.036	-0.278				
Oxygenated monoterpenes	-0.402	0.152	-0.111	-0.115	0.179	0.6137*			
Non-oxygenated Sesquiterpenes	0.318	0.353	-0.540	0.571	0.453	-0.653*	-0.380		
Oxygenated sesquiterpenes	-0.066	-0.532	0.679*	-0.598*	-0.644*	0.350	-0.165	-0.828**	
Other compounds	-0.515	0.330	0.391	-0.492	-0.632*	-0.160	-0.268	-0.026	0.145

*Significant at $p < 0.05$ **Significant at $p < 0.01$

Tabela S2. Simple correlation between the main constituents of the essential oils from leaves of *Piper gaudichaudianum* Kunth collected for the circadian rhythm study.

Rainy Season (March)								
Compound	Oxygenated monoterpenes	Non-oxygenated Sesquiterpenes	Oxygenated sesquiterpenes	Bicyclogermacrene	Eudesmadiene	<i>E</i> -Caryophyllene	α -Cadinol	Spathulenol
Non-oxygenated Sesquiterpene	0.366							
Oxygenated sesquiterpenes	-0.582	-0.854*						
Bicyclogermacrene	0.698	0.594	-0.870*					
Eudesmadiene	-0.798*	-0.554	0.843*	-0.963**				
<i>E</i> -Caryophyllene	0.723*	0.800*	-0.850*	0.774*	-0.810*			
α -Cadinol	-0.808*	-0.536	0.836*	-0.981**	0.980**	-0.806*		
Spathulenol	-0.531	-0.654	0.906**	-0.817*	0.843*	-0.656	0.787*	
<i>E</i> -Nerolidol	0.736*	0.277	-0.646	0.907*	-0.946**	0.628	-0.932**	-0.716*
Dry Season (October)								
Compound	Oxygenated monoterpenes	Non-oxygenated Sesquiterpenes	Oxygenated sesquiterpenes	Bicyclogermacrene	Eudesmadiene	<i>E</i> -Caryophyllene	α -Cadinol	Spathulenol
Non-oxygenated Sesquiterpene	0.168							
Oxygenated sesquiterpenes	-0.381	-0.954**						
Bicyclogermacrene (%)	0.524	0.818*	-0.850**					
Eudesmadiene (%)	-0.446	-0.843*	0.822*	-0.812*				
<i>E</i> -Caryophyllene (%)	-0.360	0.744*	-0.610	0.337	-0.495			
α -Cadinol	-0.413	-0.857*	0.923**	-0.795*	0.680	-0.463		
Spathulenol	-0.271	-0.926**	0.851*	-0.842*	0.944**	-0.673	0.723*	
<i>E</i> -Nerolidol	0.211	0.898**	-0.806*	0.861**	-0.823**	0.584	-0.797*	-0.932**

* Significant $p < 0.05$ ** Significant $p < 0.01$

Table S3. Database of literature on compounds and carbon skeletons of *Piper gaudichaudianum* Kunth leaves' essential oils used to determine chemophenetic variations.

Himalachane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Humulane	4.15	12.4	13.7	12	14.3	10.2	8.2	7.9	10.1	9.7	9.3	9.3	11.2	9.6	8.4
Ishwarane	10.0	3.9	4.3	3.3	1.4	2.5	4.1	2.8	3.7	5.0	4.2	3.8	6.4	1.3	3.7
Longifolane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Longipinane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Menthane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Myrcane	1.29	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pinane	1.14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Thujopsane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Reference: RO (Morais et al. 2007); RS1 - 1 to 16 (Schindler et al. 2017); RS2 (Von Poser et al. 1994); RS3 (Péres et al. 2009); RS4 (Sperotto et al. 2013); SC (Chaabani et al. 2018); SP1- 1 and 2 (Andrade et al. 1998); PR1 (Krinski et al. 2016); PR2 (Bernuci et al. 2016); PR3 - 1 and 2 (Krinski et al. 2018); PR4 (Silva et al. 2019); PR5 - 1 and 2 (Quiqui et al. 2019); PR6 (Souza et al. 2020) and; PR7 (Souza et al. 2020).

Table S3. Continuation

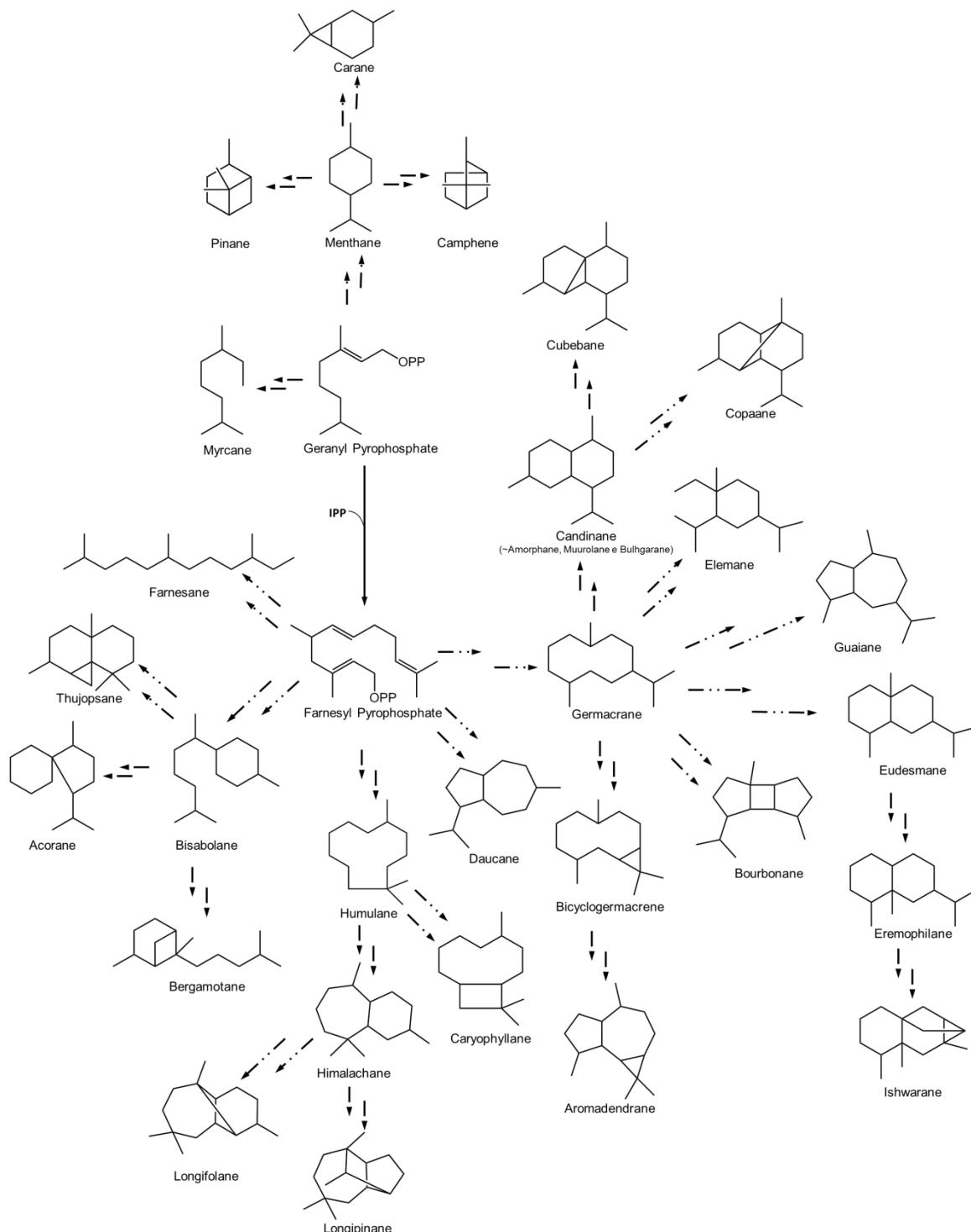
C-Skeleton	Compound	RS1 - 16	RS2	RS3	RS4	SC	SP1 - 1	SP1 - 2	PR1	PR2	PR3 - 1	PR3 - 2	PR4	PR5 - 1	PR5 - 2	PR6	PR7
Acorane	α -Acorenol												0.6				
Alkylbenzene (C3-C6)	Dillapiole		64.7														
Alkylbenzene (C3-C6)	Eugenol			0.1													
Alkylbenzene (C3-C6)	Myristicin																15.19
Aromadendrane	Aromadendrene	2.1	2.2	2.7	2.92		2.3	-						1.44	0.37		
Aromadendrane	α -Gurjunene		< 0.01	0.2	0.14									0.54	0.44		
Aromadendrane	Alloaromadendrene		7.7	3.1	3.28		0.6	4.3		2.3							
Aromadendrane	γ -Gurjunene			4.3	0.23					2.9							
Aromadendrane	β -Gurjunene			0.4										4.94	5.13		
Aromadendrane	Spathulenol	1.4	0.7	1.8	1.97		4.5	3.8		1.4				3.2	0.82		
Aromadendrane	<i>allo</i> -Aromadendrene oxide			0.00	1.1								2.47				2.47
Aromadendrane	Ledol			0.04													
Aromadendrane	Globulol		0.5	0.16		2.9	3.1	10.3					0.1				
Aromadendrane	Viridiflorol			0.6	0.18								0.21	0.2			
Bergamotane	<i>E</i> - α -Bergamotene			0.23													
Bicyclogermacrane	Bicyclogermacrene	1.2	7.4	13.16					4.4	5.12	6.39	2.57	4.15	4.81	4.63	2.57	
Bisabolane	α -Zingiberene			2.5													
Bisabolane	α -Santalene			0.33													
Bisabolane	β -Santalene			1.08													
Bisabolane	γ -Curcumene			0.12													
Bisabolane	β -Curcumene			0.52													
Bisabolane	γ - <i>E</i> -bisabolene			0.21													
Bisabolane	α -Z-Bisabolenol																
Bisabolane	Z-Calamenen-10-ol			1.5													
Bisabolane	<i>E</i> -Calamenen-10-ol				3.1												
Bisabolane	α -Bisabolol			0.02													
Bisabolane	Z- α - <i>trans</i> -Bergamotol			0.09													
Bisabolane	<i>epi</i> - α -bisabolol												1.9	1.38			

Farnesane	2-Z-6-E-Farnesol																
Germacrane	Germacrene D	1.3	2.2	0.03	4.7		1.7		1.2	1.4	1.73	1.2					
Germacrane	Germacrene B	4.2		0.37	21.5	1.1					21.53	0.4	0.21		21.53		
Germacrane	Hedycaryol			1.1													
Germacrane	Germacrene A	1.5	0.12		0.9		2.6										
Guiane	α -Bulnesene																
Guiane	α -Guaiene	0.3				8.3											
Guiane	6.9-Guaadiene								0.2	0.18							
Hidrocarbonetes	3Z-hexenol									0.3							
Hidrocarbonetes	6-Methyl-5-hepten-2-one									0.8							
Himalachane	α -Hirnachalene				3.2												
Humulane	α -Humulene	10.9	37.5	16.5	21.3	3.6	13.3	29.2	2.2		3.7	2.3	1.4		3.67		
Humulane	Epoxy Humulene II			2.5	2.3			2.8				0.9	0.51				
Humulane	Humulene oxide	1.1															
Ishwarane	Ishwarene	1.9															
Longifolane	Longifolol					1.2											
Longipinane	Longipinanol					19.1											
Menthan	Limonene	0.5	0.3	0.1		0.5	0.5					0.7					
Menthan	α -Phellandrene			0.1													
Menthan	α -Terpinene			0.1													
Menthan	γ -Terpinene			0.1													
Menthan	Terpinolene			0.1													
Menthan	α -Terpineol		0.1	0.01													
Myrcane	Myrcene	0.3	0.2								0.3						
Myrcane	Z- β -Ocimene	0.4									0.2						
Myrcane	E- β -Ocimene	0.6	0.2														
Myrcane	Linalool	4.8	0.3	0.04													
Myrcane	Geranyl acetate										5.3	5.7					
Pinane	α -Pinene	2.0	1.9	2.1					9.7	2.2	5.1		2.2				
Pinane	β -Pinene	5.6	1.2						13.2		6.6						
Thujopsane	Z-dihydro-Mayurone			1.9													
Chemical classes	Monoterpene hydrocarbons	0.0	9.4	4.5	0.1	2.1	0.5	0.5	0.0	7.1	0.0	22.8	2.2	12.9	0.0	0.0	2.2
	Oxygenated monoterpenes	0.0	4.8	0.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.3	5.7	0.0	0.0

Methane	0.0	0.5	0.8	0.1	0.0	0.5	0.5	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0
Myrcane	0.0	6.1	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.8	5.7	0.0	0.0
Pinane	0.0	7.6	3.1	0.0	2.1	0.0	0.0	0.0	0.0	0.0	22.8	2.2	11.7	0.0	0.0	2.2
Thujopsane	0.0	0.0	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

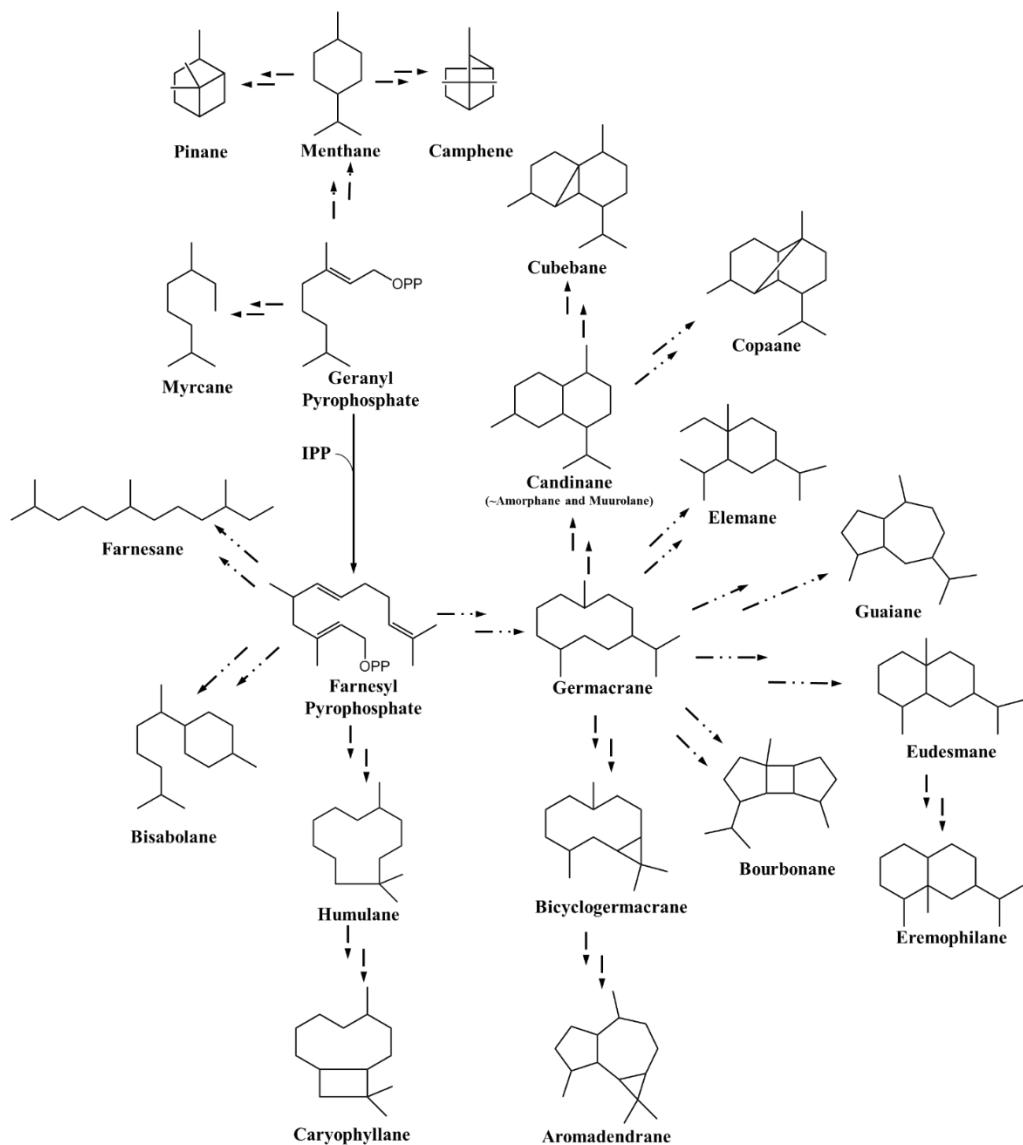
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Scheme S1. Biosynthetic map of terpene carbon skeleton types based on essential oils from leaves of from *Piper gaudichaudianum* Kunth of this study and database from literature.

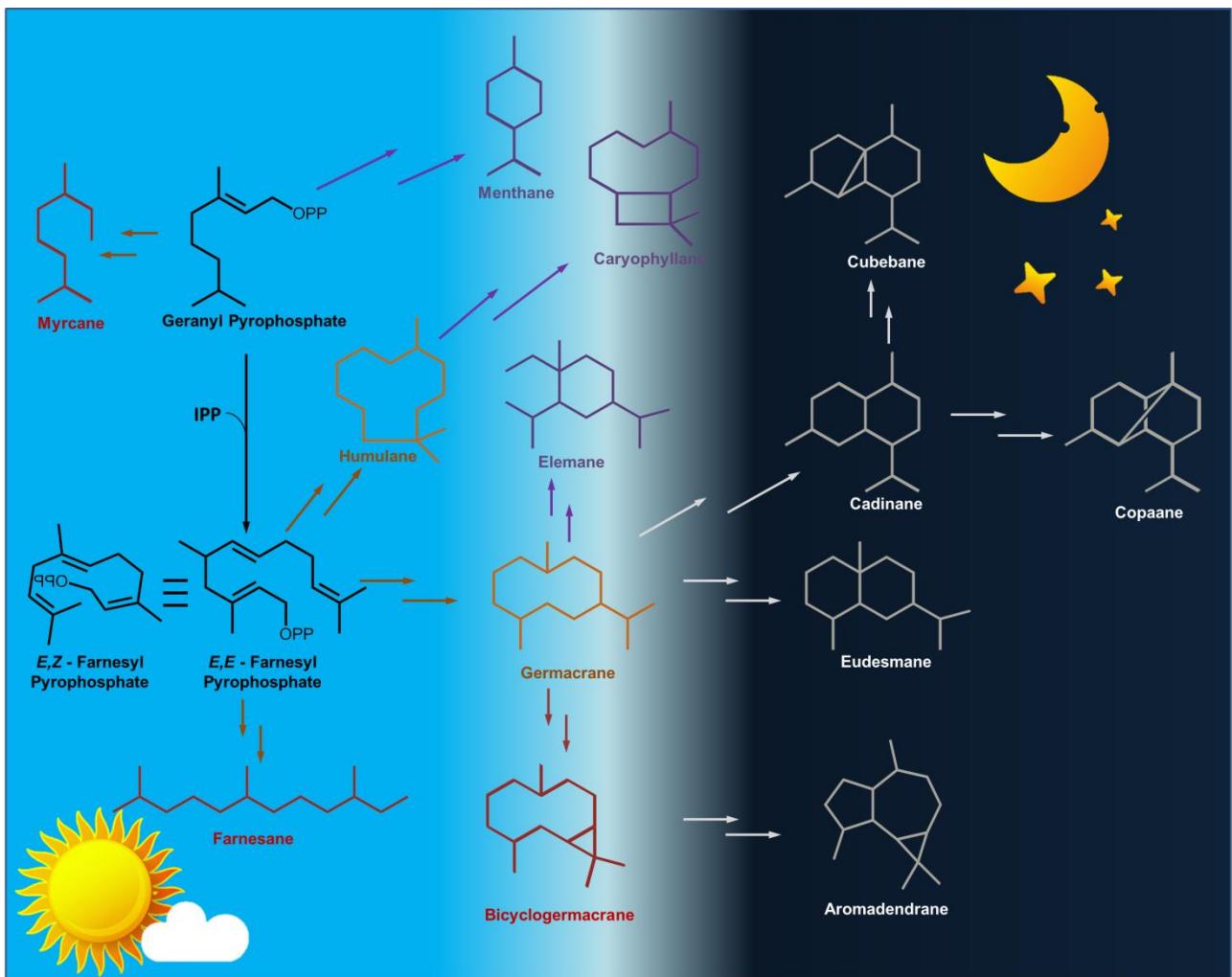


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that some steps are missed in the diagram. Broken line arrows represent a theoretical biosynthetic path that may or may not be active. Whole unbroken arrow represents a well established primary biosynthetic pathway.



Scheme S2. Biosynthetic map of terpene carbon skeleton types based on the essential oils compounds from leaves of *Piper gaudichaudianum* Kunth (Piperaceae) for seasonality studies. Double arrows indicate that some steps are missed in the diagram. Broken line arrows represent a theoretical biosynthetic path that may or may not be active. Whole unbroken arrow represents a well established primary biosynthetic pathway.



Scheme S3. Biosynthetic map of terpene carbon skeleton types based on the essential oils compounds from leaves of *Piper gaudichaudianum* Kunth (Piperaceae) for circadian rhythm studies.

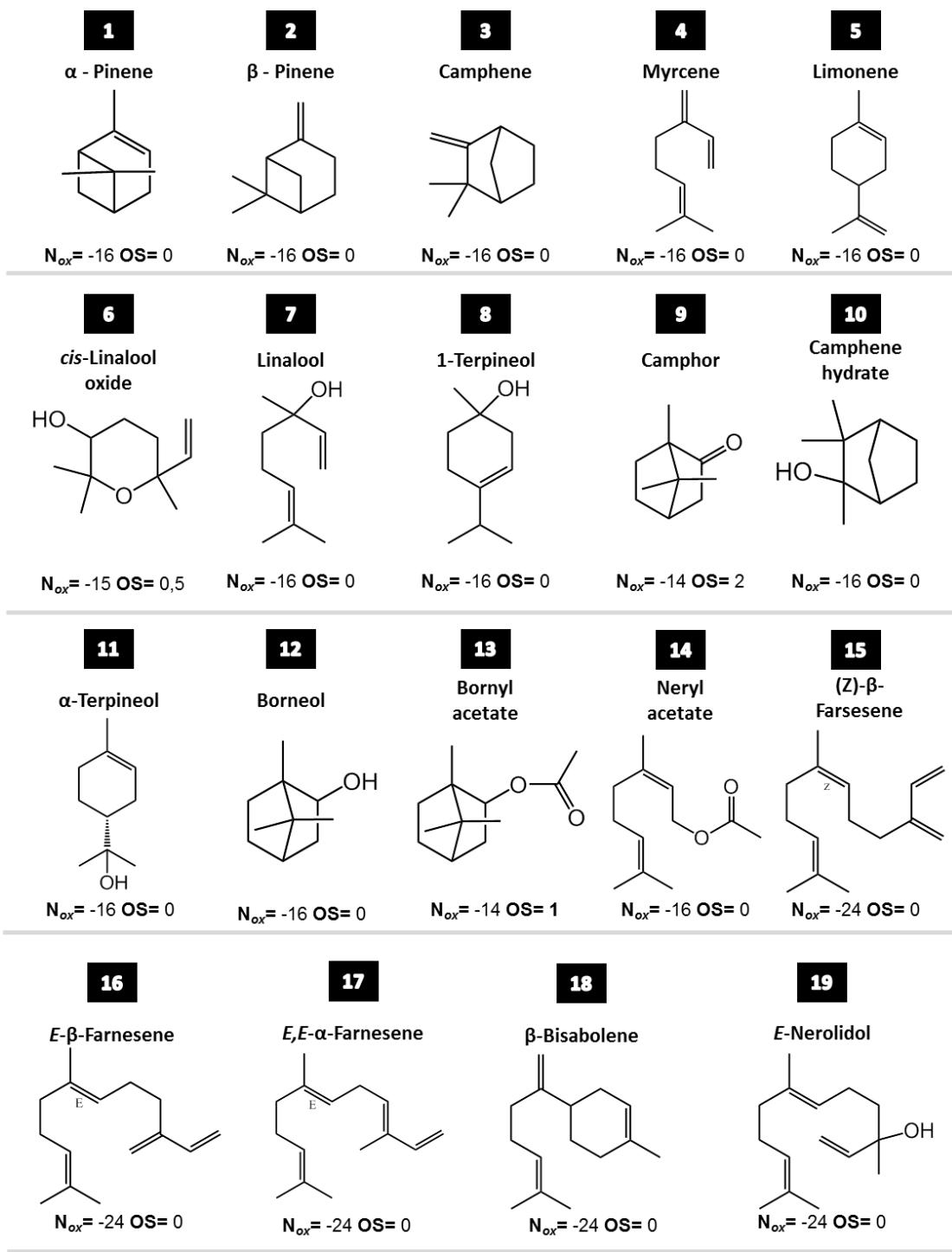


Figure S1. Continuation

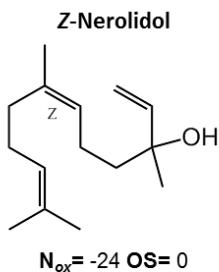
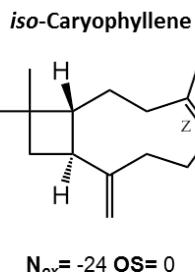
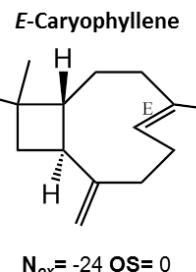
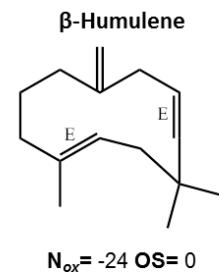
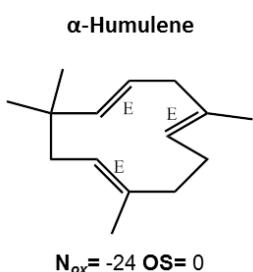
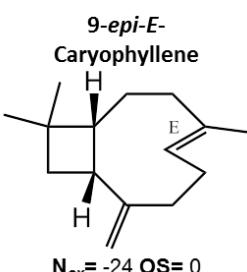
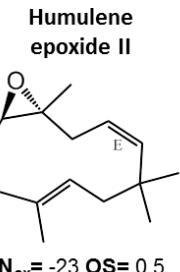
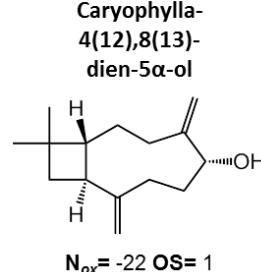
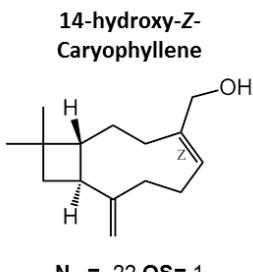
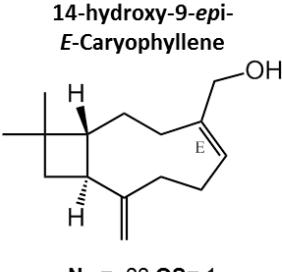
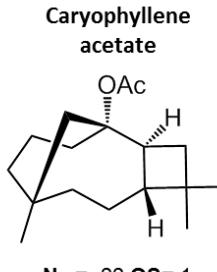
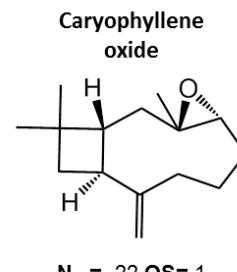
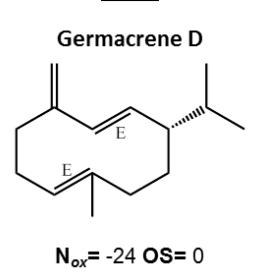
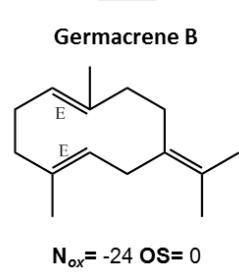
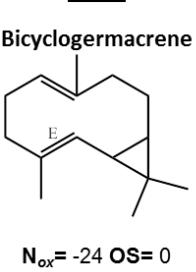
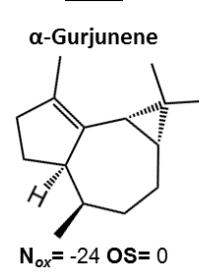
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Figure S1. Continuation

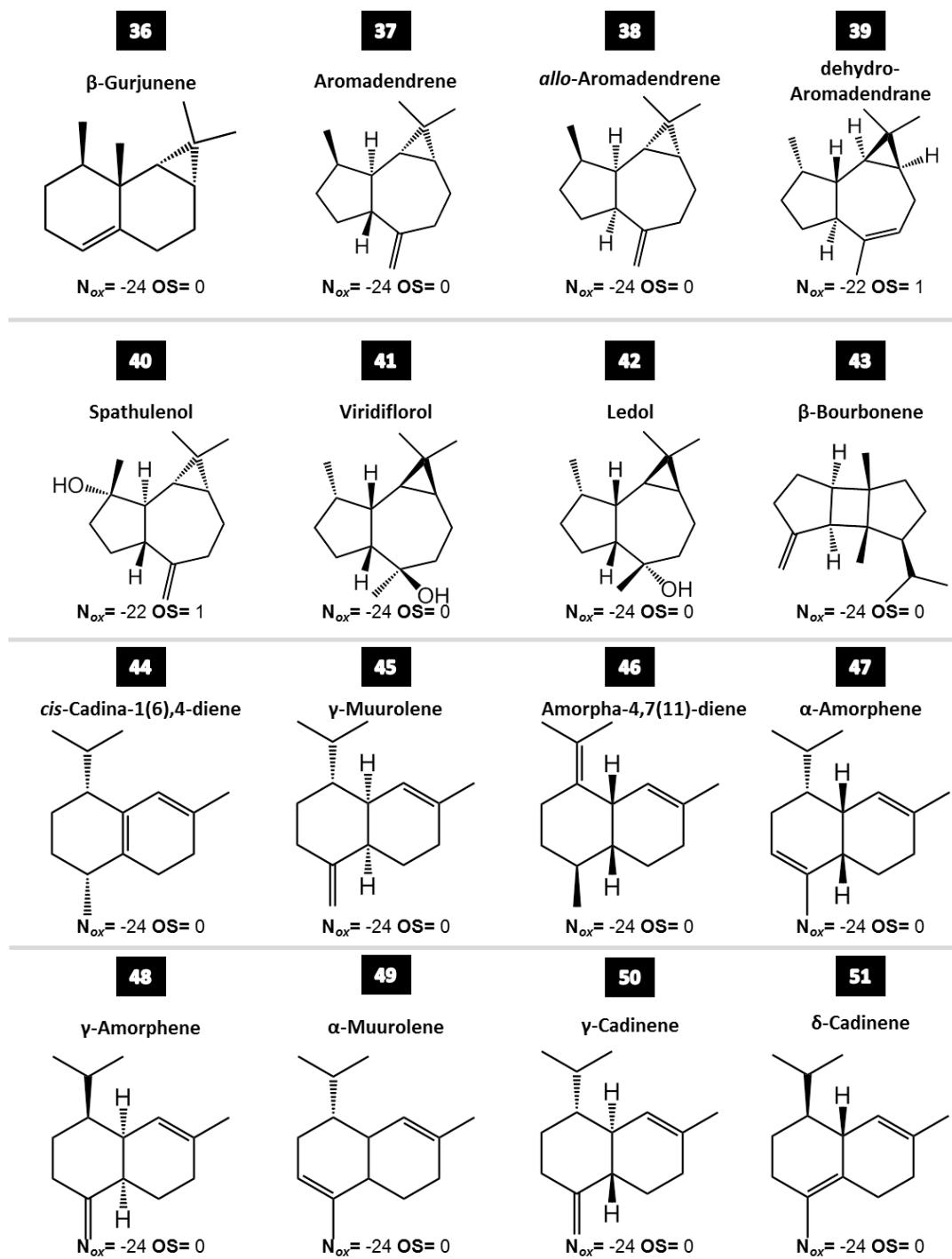


Figure S1. Continuation

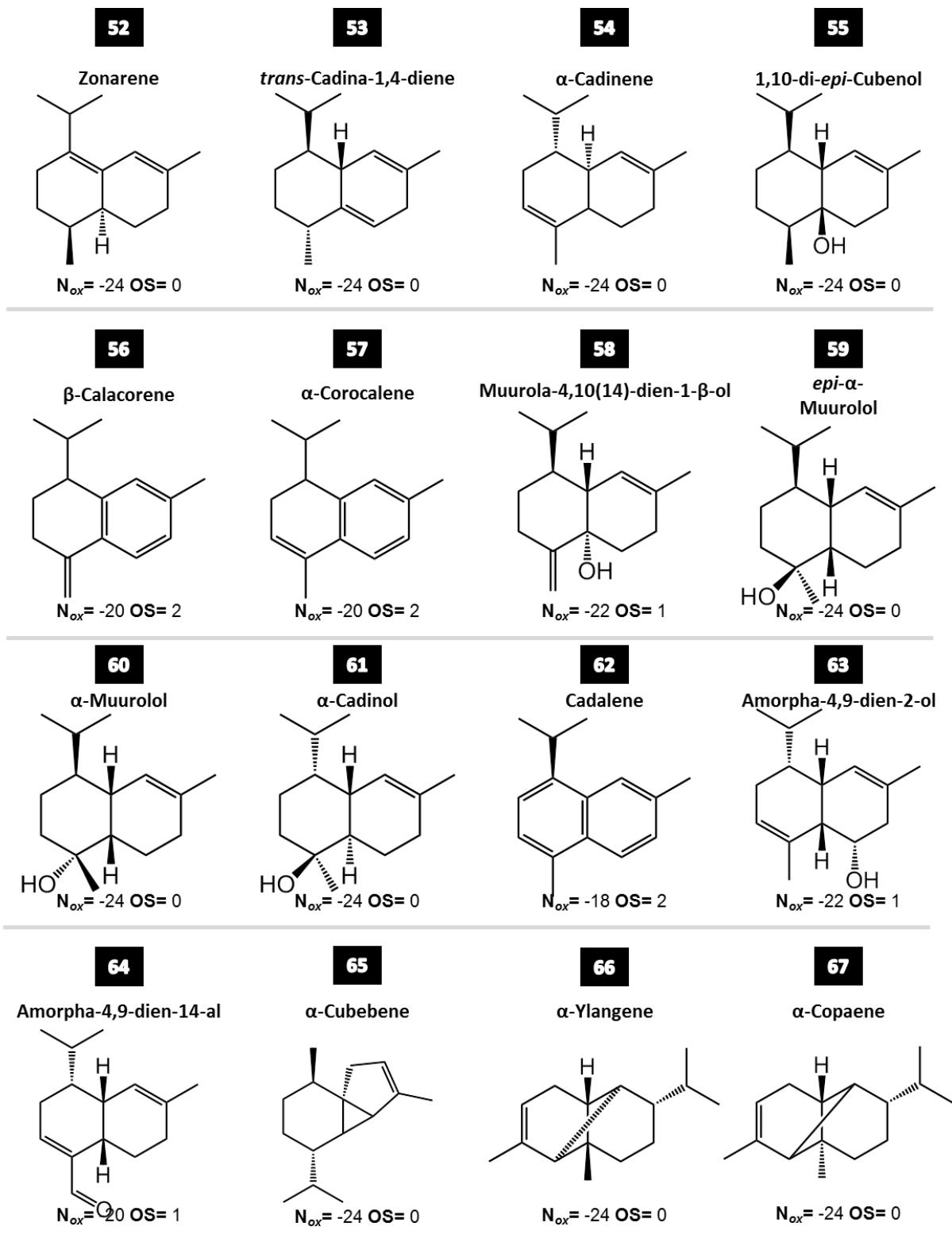


Figure S1. Continuation

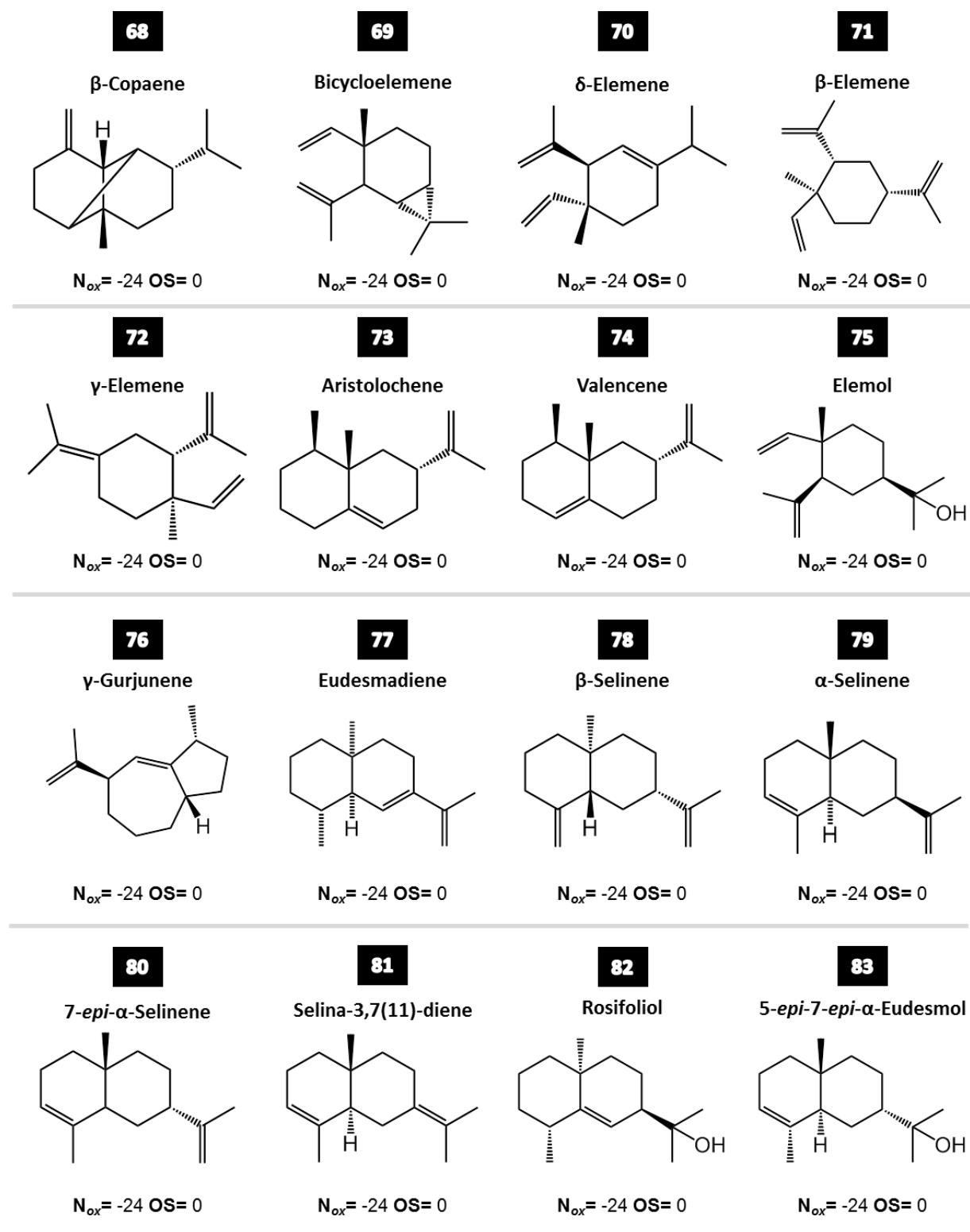


Figure S1. Continuation

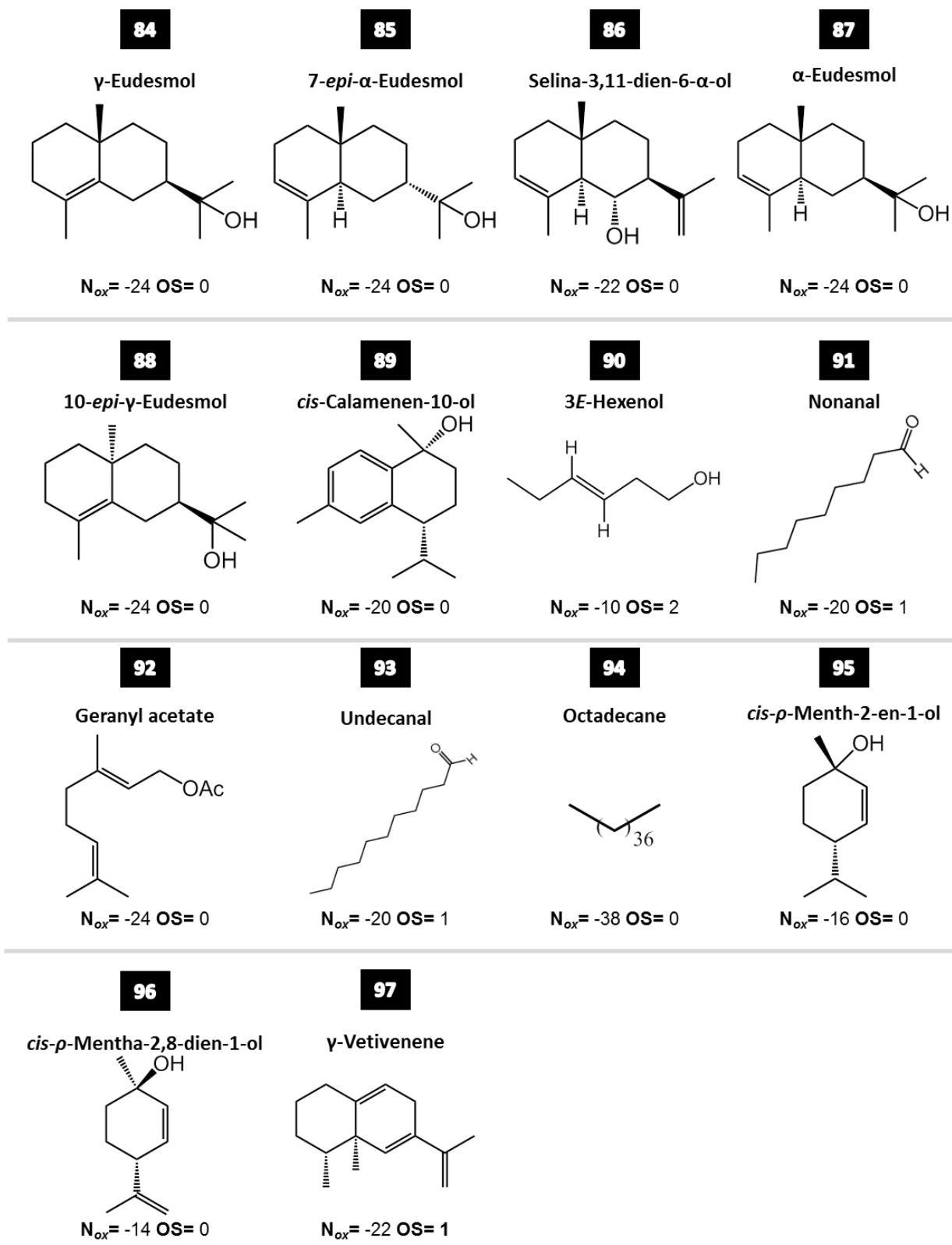


Figure S1. Structures of terpenic derivatives (monoterpoids and sesquiterpenes) and non-terpenic

hydrocarbons identified in the essential oils of *Piper gaudichaudianum* Kunth with their respective oxidation numbers (Nox) and the values of the oxidation steps (OS) of terpene-type chemical precursors.

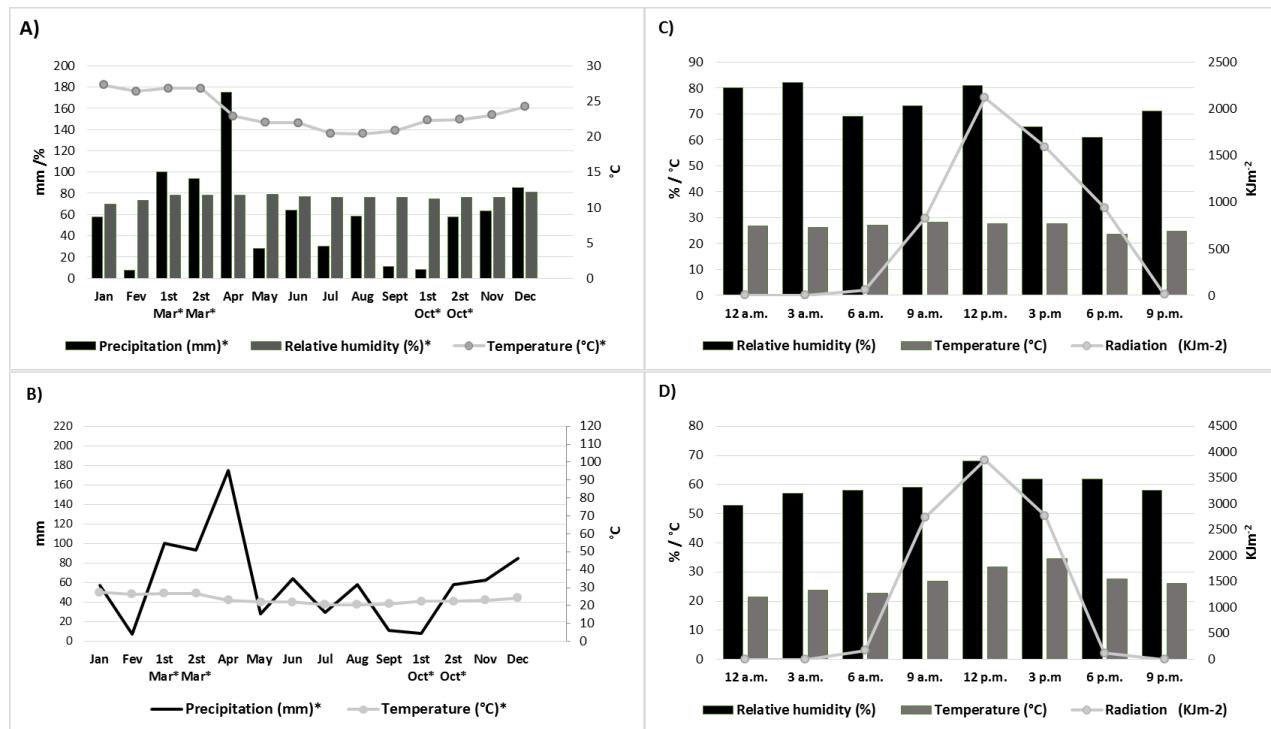


Figure S2. Climatic data of Rio de Janeiro City (Brazil) during the collections of *Piper gaudichaudianum* Kunth leaves. Data collected from reference INMET (2020). Monthly averages of temperature, precipitation, and relative humidity from January to December 2017 (A). Ombothermal diagram from January to December 2017 (B). Data of temperature, relative humidity, and radiation from the leaves' collection time for the circadian study in March (C) and October 2017 (D).