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R-(-)Linalool UV Spectroscopy: The Experimental and Theoretical Study

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Linalool (LIN) molecule is a natural essential oil used commercially in a lot industrialized products. The most these products are used commercially in hospital, pharmacologic product, etc. The utilization of theoretical methods in the analysis of essential oil derived of Amazonian plants is very small, mainly in relation to the study of its physical and chemical proprieties. In this work we will compare the UV spectra obtained by the ZINDO/S-CI and TD-DFT/B3LYP/6-311+G(d,p) methods. For our case, the TD-DFT method have shown a better description and reproducibility for the UV spectrum of R-(-)linalool molecule.

Keywords: R-(-)Linalool, ZINDO/S-CI, UV Spectroscopy, TD-DFT.

1. INTRODUCTION

The essential oils are an important class of natural products inside the great Amazonian biodiversity. The essential oils are soluble in alcohol and common organic solvent and present low solubility in water.[1] These oils are generally colorless and present low density than water, with some few exceptions. They are almost always endowed with some optic activity, with high refractive index.[1] The R-(-)linalool is a tertiary alcoholic monoterpene of open chain and can be found under the form of a mixture of isomers (Fig. 1) and it has a nonsymmetrical carbon and therefore is optically active.

This molecular specie exists in a number of essential oils, namely ho-leaf (85%), coriander (70%), and lavender and spike lavender (45%) oils.[2] Several Amazonian plants present the linalool as one of their organic compound. In the industry is used mainly in the production of perfume,[3] in the synthesis molecular (for example, the linalyl acetate[4]) and sedatives.[5] The R-(-)linalool is the main component found on Aniba duckei Kostermans species and their extractions correspond to 90% of all chemistry that compose the essential oils.[6]

Actually, the use of computational methods is an indispensable tool for the understanding of the physical and chemical properties of molecules, mainly related to its use in biological systems. The utilization of theoretical methods in the analysis of derived compounds of Amazonian plants is very small. In this work, we study the theoretical UV absorption spectra of R-(-)linalool to understand the absorption bands, providing information about the variation of the most intense bands in the absorption spectra to this molecule by theoretical methods. The experimental spectrum of the R-(-)linalool was obtained using absorption spectrophotometer (SPP) for a small region of the theoretical spectrum, due to limitation of the equipment.

2. METHODOLOGY

2.1. Theoretical

The molecular modeling software program used for this study was Hyperchem7.5 program (HypercubeInc., Gainsville, FL)[7] to the PM3 semi-empirical method to carry out the optimized geometry and the *Z*-matrix served as entrance to obtained the absorption spectrum by ZINDO/S-CI (ZERNER's Intermediate Neglect of Differential Overlap-spectroscopy/Configuration Interaction). The geometry obtained by the PM3 method was refined with an hybrid B3LYP density functional, corresponding to the combination of the Becke's three-parameter exchange functional (B3)[8] with the Lee-Yang-Parr fit for electron correlation (LYP)[9] level with 6-311+G(d,p) base set with the Gaussian 03 packages.[10] The UV spectrum was obtained by use the Gausssum 1.0 program[11] for a

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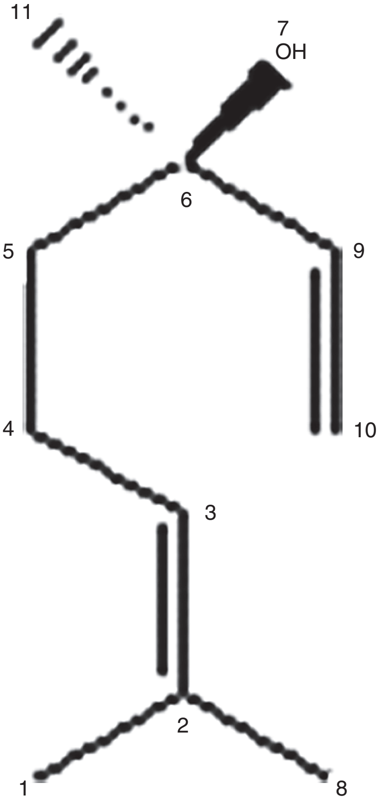

Fig. 1. Molecular structure of the R-(-)linalool and its respective carbon.

full width at half maximum (FHWM) of Gaussian peak at the 0.6 eV to both methods.

2.2. Experimental

The liquid sample of R-(-)linalool used for experimental analysis and its extraction process is described by Ref. [6]. The experimental absorption spectrum of R-(-)Linalool in the 190–250 nm regions at room temperature was obtained by using a Perkin Elmer Lambda 9 UV-VIS-NIR Spectrophotometer, with a resolution of 1.0 nm. The measurement was performed with the sample as a thin film (about 10 μm of thickness) between two parallel quartz laminas. A small amount of the R-(-)linalool was deposited between two quartz lamina (form of sandwich) submitted at the pressure to produce a thin film.

3. RESULTS AND DISCUSSION

We will present a study on the linalool for being the only sample that we had available to analyze. Our main objective is to understand which better method describes the spectrum of UV inside the two methods more used. The choice of the base for TD-DFT followed the same criterion of choice. In the Table I summarize the bond lengths corresponding to the equilibrium conformation obtained for different basis set.

Concerning bond distances (Table I), the B3LYP/6-31G(d) basis set has calculates the longest values for all, except to bond length C5-C6 and duple bond. We can also observe that bond distances are shorter to semi-empirical method and shorter when going from 3-21G to 6-31G(d) and 6-311 + G(d,p) for density functional. The reduction for the bond distance values to be associated to the combination of diffuse and polarization functions.

Table II summarize the bond angles corresponding to the equilibrium conformation obtained for different basis set. We can observe that the bond angles from 6-31G(d) to 6-311 + G(d,p) is possible observe that the effect of the addition of diffuse and polarization functions is not of great importance. For the angle values calculated by HF/6-31G(d) and B3LYP/3-21G, we observe that HF angles are shorter, but it has bond angles close to the B3LYP/6-31G(d) and B3LYP/6-311 + G(d,p), except for three bond angles: (C1,C2,C3), (C1,C2,C8) and (O7,C6,C9).

Concerning bond angles for the semi-empirical method, we can observe that all bond angle values are lowest, except to angle (C1,C2,C8), (C3,C2,C8), (C5,C6,C7) and (O7,C6,C9) that present values highest. Table II present values for bond angles by the Hartree-Fock method are very similar with respect to the density functional for the 6-31G(d) and 6-311 + G(d,p) basis set, but different for the bond lengths.

Figure 2 show the experimetnal spectrum for the R-(-)linalool that present a peak with maximum intensity

Table I. Bond lengths (in angstron) for R-(-)linalool for different basis set.

	Length				
Bond	PM3	HF/6-31G(d)	B3LYP/3-21G	B3LYP/6-31G(d)	B3LYP/6-311+G(d,p)
C1–C2	1,4859	1,5100	1,5171	1,5098	1,5083
C2–C3	1,3395	1,3256	1,3399	1,3429	1,3403
C2–C8	1,4880	1,5106	1,5194	1,5109	1,5095
C3–C4	1,4862	1,5111	1,5144	1,5089	1,5080
C4–C5	1,5242	1,5401	1,5525	1,5461	1,5451
C5–C6	1,5484	1,5390	1,5427	1,5451	1,5441
C6–O7	1,4305	1,4216	1,4861	1,4490	1,4534
C6–C9	1,5138	1,5169	1,5141	1,5168	1,5155
C6–C11	1,5342	1,5287	1,5353	1,5335	1,5317
C9–C10	1,3268	1,3193	1,3331	1,3347	1,3317

Table II. Bond angle (in degree) for R-(-)linalool for different basis set.

	Ângulos				
Bond	PM3	HF/6-31G(d)	B3LYP/3-21G	B3LYP/6-31G(d)	B3LYP/6-311+G(d,p)
(C1,C2,C3)	123,7571	125,2101	125,0978	124,8554	124,8543
(C1,C2,C8)	115,1765	113,9096	113,8544	114,3105	114,3116
(C3,C2,C8)	121,0663	120,8799	121,0472	120,8335	120,8335
(C2,C3,C4)	124,7072	127,7021	126,8551	127,4728	127,4717
(C3,C4,C5)	112,3706	115,7978	113,6889	115,7576	115,7576
(C4,C5,C6)	114,3498	118,7578	116,6998	118,3940	118,3928
(C5,C6,C7)	104,6868	102,8617	101,3326	102,5913	102,5916
(C5,C6,C9)	109,9682	112,0635	112,4737	112,1783	112,1781
(C5,C6,C11)	110,6600	111,8420	112,2120	111,8873	111,8876
(O7,C6,C9)	108,4583	106,9920	106,7090	106,6935	106,6940

($\lambda_{\max}$) to 207 nm, corresponding to the transition $\pi \rightarrow \pi^*$. Due to limitation of the equipment we cannot observe the behavior for wavelengths below of 190 nm. The maximum absorption ($\lambda_{\max}$) is due to presence of composed aliphatic unsaturated with its double bond, due to the participation of the orbital with double bond of the carbon.

The theoretical spectrum (Fig. 3) present values for maximum absorption ($\lambda_{\max}$) at ~175 and ~206 nm to TD-DFT and ZINDO/S-CI, respectively. What represents a relative error of the measure of ~14.36% of the experimental data for density functional. This difference be associated to the intermolecular interaction between the molecules of linalool, producing a displacement with respect $\lambda_{\max}$ to larger wavelengths. In the Figure 3 the two maximum absorption ($\lambda_{\max}$) are of the type $\pi \rightarrow \pi^*$ to both methodology, with a strong contribution of the double bond in the HOMOs orbital, whereas for the LUMOs orbital the bigger contribution is for the double bonds of carbon presents in the molecule.

The density functionary does not describe with good precision the absorption spectrum for linalool in its liquid form. This effect is probably due the molecular interaction caused by Hydrogen Bridge, but qualitatively it presents one better description of the transitions. The method semi-empirical presented better resulted for molecule of linalool due to its spectroscopic parameters that take in

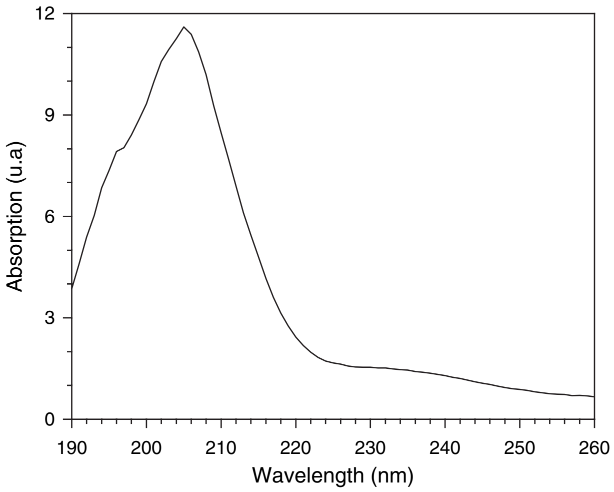

Fig. 2. Experimental spectrum of the R-(-)linalool, without solvent, for the region of 190 to 270 nm with $\lambda_{\max} = 207$ nm.

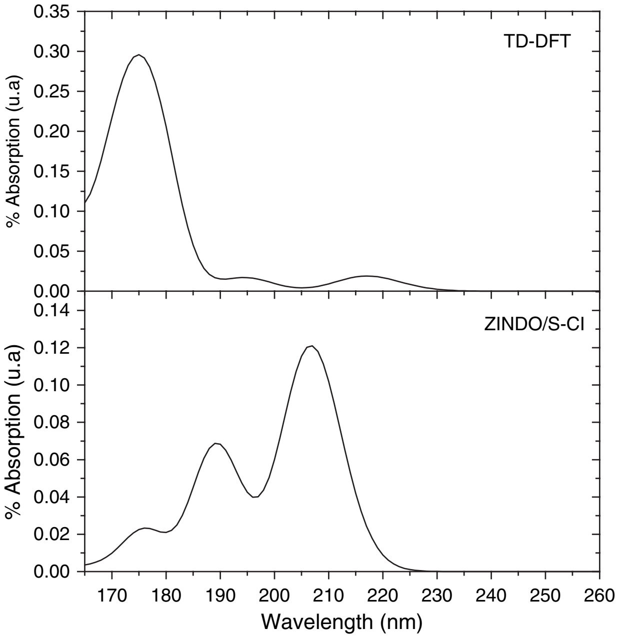

Fig. 3. Theoretical absorption spectrum to the 190 to 270 nm regions, using TD-DFT and ZINDO/S-CI methods.

Table III. Excitations wavelengths and electronic transitions of the R-(-)linalool using semi-empirical method.

Wavelength (nm)	Major intensity	Minor intensity
206	HOMO->LUMO (47%), HOMO->L + 1 (44%)	H − 1->L + 1 (− 2%)
189	H − 1->LUMO (44%), HOMO->LUMO (17%) HOMO->L + 1 (− 25%),	H − 1->L + 1 (− 7%)
176	H − 1->LUMO (36%), HOMO->LUMO (−30%), HOMO->L + 1 (22%)	H − 1->L + 1 (− 5%), H − 1->L + 2 (− 2%)

consideration the different types of bond (σ and π bond) in the molecule.

The Table III gives us the principal electronics transitions of the ZINDO/S-CI method that present resulted closer to the experimental data with a difference of 1 nm only. The results show that the most intense peak (206 nm) to the absorption spectra is due to the contribution of transition between HOMO and LUMO and LUMO+1 orbital.

4. CONCLUSIONS

The molecular structures of linalool have been optimized using semi-empirical and density functional level of theory. We have determined the distance and angle between the carbon and oxygen. Thus, we have shown that the values of bond lengths and bond angles of he linalool depend on the basis set used for the density functional calculations. For the semi-empirical method basically all results are smaller than density functional method, except for some angles. The values for bond angles by the Hartree-Fock method are very similar with respect to the density functional for the 6-31G(d) and 6-311+G(d,p) basis set, but different for the bond lengths. In this study, the semi-empirical method present better results in relation to the experimental spectrum. Unfortunately, we do not get the experimental structure to analyze our theoretical distances and angle on molecule.

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