Plant Archives Vol. 19, Supplement 2, 2019 pp. 327-332 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

LIGNIN FT-IR STUDY OF IRAQI DATE PALM *PHOENIX DACTYLIFERA* FROND BASES WOOD

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Abstract

Date palms *Phoenix dactylifera* trees have played an important role in Iraq. Thousand tons of date palm fronds wood waste is discarded daily. Thus, there is an urgent need to discover methodical database for Iraqi phoenix date palm fronds wood that open the door to suitable application for this waste. Extraction and purification of lignin for 5 kinds of Iraqi date palm testers (Phoenix -Gibgab, Phoenix- Bint-Swelih, and Phoenix - Mtawag, Phoenix-Ohm-Al-Blales, and Phoenix- Hillawi) by means of Klason lignin technique has been done. Weight of extracted lignin within range of (0.4430 - 0.6411) g., and % lignin range of (22.15– 32.05). Oils, waxes, resin along with proteins of wood gums percent of are of (17.35 – 30.30) range. The characterization of FT–IR has depicted that the (-OH) phenolic cluster come into sight in Ohm-Al-Blales and Hillawi lignin's structures and vanish in another lignin types, while Aromatic ether aryl (4-O-5 inter monomeric lignin connection disappear in Bint-Swelih lignin structure and come into sight in another lignin types. Also Alkyl substituted ether (O - CH_3 or O – CH_2 stretch) come into sight in Gibgab and Ohm-Al-Blales lignin's structures and vanish in another lignin types, while Vinyl ether (in phase C- O - C stretch) appear in Bint-Swelih and Hillawi lignin's structures and vanish in other lignin types. UV /Vis. Investigation has depicted that the lowermost absorbing at small wave length (228 nm) is for Gibgab lignin, whereas the uppermost absorbing at small wave length (231 nm) is for Mtawag lignin. Also, the lowest absorbing at long wavelength (274nm) is for Gibgab lignin, while the uppermost absorbing at long wave length (270 nm) is for Mtawag lignin.

Keywords: Analytical profile; Date palm; Lignin; Iraqi *Phoenix dactylifera*; Trees.

Introduction

Date palm (*Phoenix dactylifera* L.) stands for highly efficacious and imperative crop in the warm and dry areas as in Egypt Emirates, Saudi Arabia and Iraq (Chao *et al*.; 2007). Date palm products in these countries are frequently consumed for human and animal ingesting, drugs, make-ups, woodworking, and kindling. *Phoenix dactylifera* date palm agronomy is appropriately conventional in the Middle East, particularly in Mesopotamia regions of Iraq where watering is obtainable. Significantly, Iraq stands for the (*Phoenix dactylifera* L.) origin, where about 22.3 million trees are cultivate and greater than one million people for their living rely on its farming or trade (Rattan and Abdul-Haffiz, 1980). The most widespread date palm trees traditional operations implemented in plantations include dehorning, pollination, fruit thinning, pruning and bagging of bunches, bending and pesticide control (Shamsi and Mazloumzadeh, 2009). Pruning process stands for the choosy elimination of any hanging, dead or harmful fronds to uphold date palm trees healthy to have a high quantity and good quality of date fruits (Approved American National standards, 2008). For that reason, it is imperative to investigate the content of the biological waste resultant from the pruning, as the date palm fronds is the entryway and exit of chemicals from and to the trunk of the palm. Fronds wood is soft; plant cell walls principally have 4:3:3 ratios of cellulose, hemicellulose, and lignin. This proportion varies depends on its sources like softwood, hardwood in addition to herbs. In addition, biological lignocellulose constituents have a trivial quantity of nitrogenous and pectin compounds as well as the secret ash. For example, the elemental wood content has approximately 50 percent of carbon, 6 percent of hydrogen, and 44 percent of oxygen besides 0.05–0.4 percent of nitrogen (Zhang *et al*., 1997). The plant cell wall structure is compacted. There is dissimilar bonding between hemicellulose, cellulose in addition to lignin. They are essentially combined through a hydrogen bond and chemical. The chemical bonds amid the lignin and hemicellulose principally imply the chemical bonds among residues of Galactose, remainders of arabinose on the sideways of chains of hemicellulose molecules besides lignin (Chen, 2006 & Yang, 2008). Cellulose stands for significant constituents in a plant cell wall that regulates the wall arrangement. It stands for organic extreme molecular polymer that has glucose remainders, with cellobiose as the elementary coupling component. It as well represents highly abundant renewable source in nature. Extra significant constituent in a cell wall is lignin that stands for a polyphenolic polymer with 3 D network. Excepting cellulose, it stands for, in the cell wall, highly abundant large-molecule polymer. Derivatives of Phenylpropanoid stand for the elementary components of the lignin. They are combined into high molecular materials through carbon- carbon bonds or ether bonds. In relation to the substantial features, lignin is rigid, that upsurges the cell wall hardness. Generally, a plant cell wall that supports functional and mechanical action has extraordinary lignin amount. The amount of Lignin has been approximately 27–32 percent of in wooded plants and approximately 14–25 percent of in herbaceous plants (Chen *et al*., 1996). Between every basic unit, the modes of coupling involve ß-O-4, ß-5, ß-1, and so on. In lignin, ether bonds involve alkyl-ether bonds, phenol-ether bonds, dialkyl bonds, diaryl ether bonds. Approximately dual thirds to three for quarter phenyl-propane units of lignin can be associated to neighboring physical units through ether bonds. The minor portion only exists in a form of free phenolic hydroxyl. Phenol- ether bonds comprise 70–80 percent of in these clusters, guaiacyl glycerol-"ß-aryl ethers (ß-O-4) comprise approximately half of phenol-ether bonds, and subsequently guaiacyl glycerol-'α-aryl ethers ('α-O-4), likewise having another categories of ether bonds. Lignin has principally aryl glycerol-ß-aryl-(ß-O-4) ether bonds, roughly 50 percent of lignin in softwood and greater than 60 percent of in hardwood. A dominant coupling type is ß-5, ß-ß connection in C–C bonds of lignin, after that ß-1, ß-2, 5–5, and so on (Fig. 1) (Tao YZ., Guan

YT., 2003) The main bond types are about eight links cause the existence of different types of lignin in dissimilar kinds of date palm frond woods. Categorization and determination of these links kinds of lignin represents the objective of this paper. Correspondingly the determining oil, wax, feasibly several percentages of wood gums and resins fractions in 5 diverse categories of Iraqi *Phoenix dactylifera* Date palm pruning woods is presented. Lignin characterization was done by U.V., and FT-IR spectrum (Hilal *et al*., 2013).

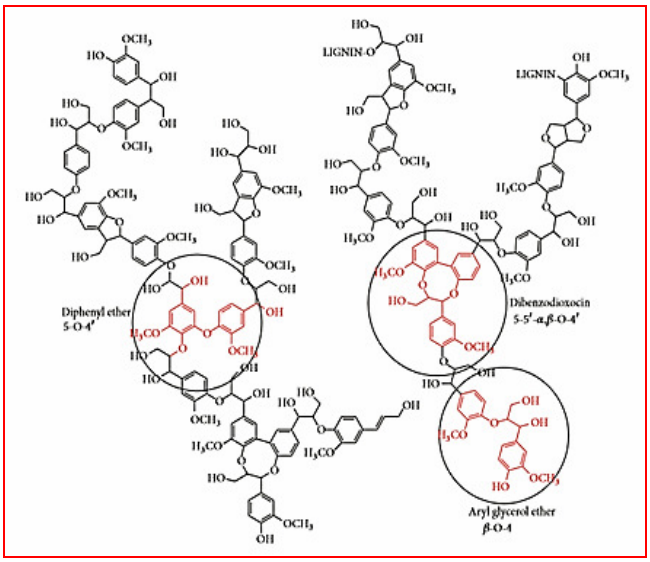


Fig. 1: Common chemical structure of lignin

Materials and method

Quantitative determining of oil, lignin, gum, protein and waxes of Iraqi date palm frond bases woods.

Here, 5 dissimilar kinds of Iraqi palm fronds wood testers (Phoenix -Gibgab, Phoenix- Bint-Swelih, Phoenix - Mtawag, Phoenix-Ohm-Al-Blales, and Phoenix- Hillawi) were examined using Klason sulfuric acid Lignin technique. Equal weight wood tasters have been extracted with solution of alcohol-benzene mixture 1:1, (low boiling point solvent), to remove waxes, oils, some resins, and feasibly several portions of wood gums presented for evading a contamination in lignin remainder (Peter *et al*., 1998). The pretreatment technique has been briefed as follow: Exactly 2 grams of air-dehydrated pruning wood powder of 60 to 100 mesh have been considered in a tared alundum crucible (the crucible and its substances have been dehydrated to fixed weight at 105° C and then cooled and weighed. At that point, it extracted for 4 hrs. in Soxhlet tool with 150 ml of alcohol-benzene solution mixture. Then, the solvent has been uninvolved and washed through suction to eliminate the benzene residue. Afterward, it extracted by 400 ml hot distilled water for 3 hours in the water bath, cleaned with boiling distilled water and ethanol. Lastly, it was dehydrated. At that moment, weigh the dried remainder correctly to evaluate the ratio of Oil, Waxes, Protein and Gums in every tester depicted in Table 1. A dehydrated remainder has been hydrolyzed by stirring and well mixing at room temperature (25 ± 1 °C) with 25 ml of 72 percent of Sulfuric acid (H_2SO_4) for 2 hours, then the resultant mixture has been diluted with 575 ml distilled water to make 3 percent of acid solution, and heated for 4 hours under Reflux Condenser. A hydrolyzed residue was filtered on a tared alundum Crucible, cleaned for free acid using hot distilled water, and then dehydrated, and balanced. The lignin percentage lignin has been computed based on oven-dehydrated tester illustrated by Table 1.

Table 1: Quantitative determined details of diverse kinds of IRAQI Phoenix date palm fronds wood Lignin.

No.	Tester name	Tester wt. (g.)	Tester wt. after handling with Benzene- alcohol mixture (g.)	Tester wt. after handling with 72 percent of H_2SO_4 (g.)	Waxes, Oils, Resins, and Gums percent of	Wood Lignin percent of
1	Phoenix -Gibgab	2	1.4503	0.4430	27.48	22.15
2	Phoenix- Bint-Swelih	2	1.3939	0.6411	30.30	32.05
3	Phoenix – Mtawag	2	1.653	0.4557	17.35	22.75
4	Phoenix – Ohm-Al-Blales	2	1.4358	0.4742	28.21	23.71
5	Phoenix- Hillawi	2	1.422	0.5290	29.70	26.45

Lignin characterization

The 5 isolated dehydrated lignin testers have been categorized through FT –IR spectroscopic investigation based on Shimadzu FTIR Spectrometer. Spectrophotometric analysis has been by means of UV – 1800 Shimadzu Spectrophotometer.

Results and Discussion

Quantitative Determining of Lignin

Lignin extraction yield of the 5 dissimilar kinds of IRAQI Phoenix Date palm frond bases (2g.) wood testers under 0.443 to 0.6411 g range, and the lignin percentage from 22.15 – 26.45 have been depicted in Table 1. Also the highest lignin percent of has been in Bint-Swelih Wood, and the lowermost lignin percentage has been in Gibgab Wood. Another ingredients (Waxes, Oils, resins and Gums) have been percentages under (17.35– 30.30) range, where the lowermost percentage has been for Mtawag Wood, and the maximum percentage has been for Bint-Swelih Wood.

Characterization of lignin

Characterization of FT–IR

Under study, extracted lignin from frond bases date palm wood testers have shown converged absorbing peaks on FT-IR spectra which has been interpreted in (Table 2) deriving from Figures (3 – 7). A stretched vibration absorbing of (-OH) cluster has presented also converged peaks of robust intensities for all investigated testers which indicates that each investigated testers lignin have high level of (-OH) cluster in its structure. Furthermore, a stretching vibration absorbing of - C-H aliphatic cluster presented converged peaks of robust intensities for each investigated tester, and that is due to advanced concentrations of monomers in lignin configuration of investigated testers. A stretching vibration absorbing of conjugated carbonyl cluster presented converged peaks for each investigated sample with low intensity peak for Mtawag lignin & Ohm-Al-Blales lignin and strong intensity peak for the other testers, due to its existence at a low to strong concentration in investigated

testers. The stretched vibration absorbing of aromatic rings along with (-C=C-C-and –C=C-C=C-) or (β-1, β-β, 5-5, and β-5 inter monomeric lignin connection) presented converged peaks of robust intensities for each investigated tester excluding Bint-Swelih lignin presented feeble intensity peak at 1604 cm^{-1}, attributable to the occurrence of these connections recurrently in each investigated testers, excluding Bint-Swelih lignin structure. (C-H) deforming and aromatic ring vibration presented converged peaks of robust intensities for each investigated tester. Bending vibrations absorbing s of -OH have no absorbing peaks for Gibgab lignin, Bint-Swelih lignin, & Mtawag lignin, but Hillawi lignin presented feeble intensity peak at 1384 cm^{-1}, also Ohm-Al-Blales lignin presented sensible intensity peak at 1384 cm^{-1}. Namely, -OH phenolic cluster vanish in 3 lignin testers because of the possibility of free essential midway creation from -OH phenolic cluster position that ingest the clusters for ether connections. An aromatic ether aryl (4-O-5 inter monomeric lignin connection) presented converged peaks of resilient intensity peaks for (Gibgab lignin at 1273 cm^{-1}, in addition to 1219 cm^{-1}), along with (Mtawag lignin at 1274 cm^{-1}, and moderate intensity peak 1221 cm^{-1}) testers, moderate intensity concerning (Ohm-Al-Blales lignin at 1273 cm^{-1}, and 1217 cm^{-1}), Bint-Swelih lignin has no absorbing peaks. Namely, (4-O-5 inter monomeric lignin connection) likelihood is greater in Gibgab, and Mtawag lignin's structures. A stretching vibration absorbing of cyclic ether of huge ring stretching (DODO inter monomeric lignin connection) has presented converged peaks of robust intensities for each investigated tester. This specifies its strong presence probability in all categories. The stretched vibration absorbing of alkyl substituted ether (O – CH_3 or O – CH_2) presented dual converged peaks of moderate intensity for Ohm-Al-Blales lignin at 1165 cm^{-1}, and feeble intensity concerning Gibgab lignin at 1165 cm^{-1}. This signifies for that alkyl substituted ether (O – CH_3 or O – CH_2) vanish in Bint-Swelih, Mtawag, and Hillawi lignin's structures as a result of the likelihood of free fundamental midway creation from ether (O – CH_3 or O – CH_2) position that ingest the clusters configurations for another sorts of ether connections. A stretching vibration absorbing of vinyl ether in (C- O - C stretch.) phase presented converged peaks of feeble intensity for Gibgab lignin at 848 cm^{-1} and moderate intensity concerning Mtawag & Ohm-Al-Blales lignins with no absorbing for Bint-Swelih lignin that might signify for its occurrence at a minor concentrations in each feasible lignin configurations.

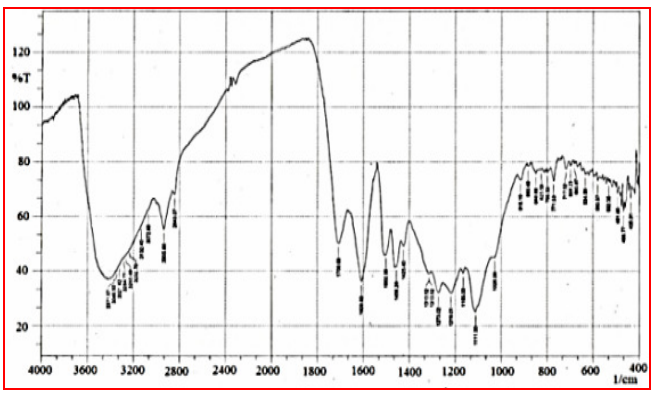


Fig. 3: Lignin FT – IR band of Phoenix – Gibgab.

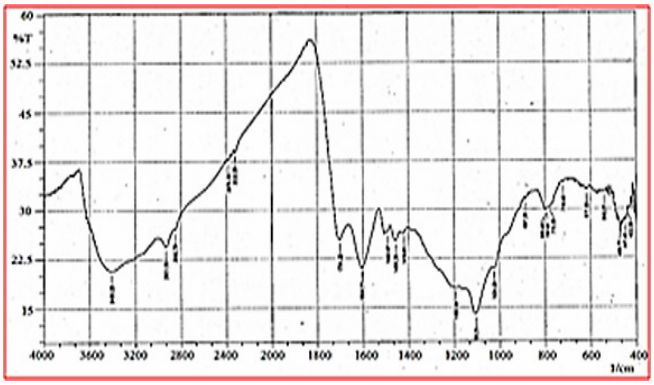


Fig. 4: Lignin FT – IR band of Phoenix – Bent Sweleh.

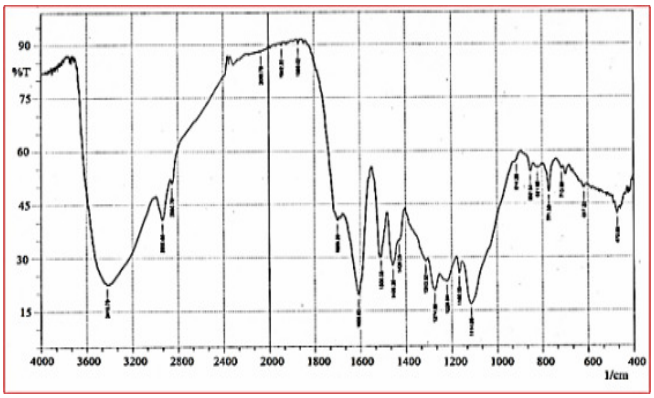


Fig. 5: Lignin FT – IR band of Phoenix – Mtawak.

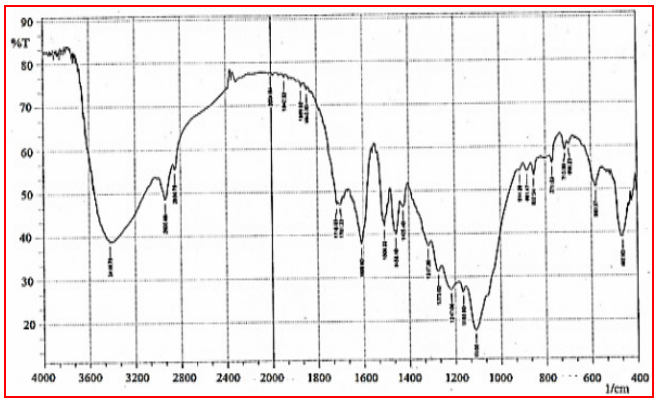


Fig. 6: Lignin FT– IR band of Phoenix – Ohm Alblaliz.

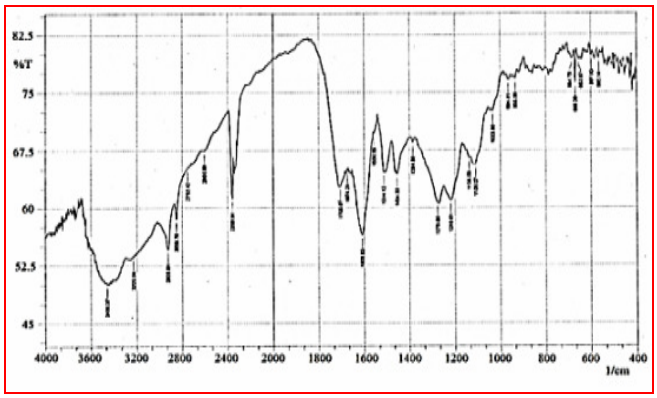
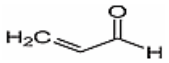
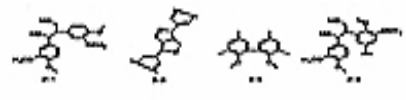
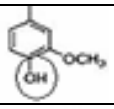
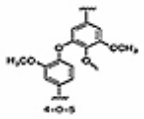
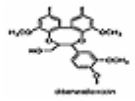
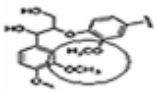
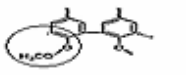


Fig. 7: Lignin FT – IR band of Phoenix – Hillawi.

Table 5: Peaks of FT-IR of lignin and it's inter monomeric connections

Vibrational clusters and comments	Inter monomeric lignin connection configuration	Phoenix - Gibgab lignin	Phoenix - Bint-Swelih lignin	Phoenix - Mtawag lignin	Phoenix- Ohm-Al-Blales lignin	Phoenix – Hillawi lignin
		Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}
-OH stretching vibration		3371(s)	3408 (s)	3419 (s)	3419 (s)	3458 (s)
C-H stretching vibration		2935 (s)	2931 (s)	2935 (s)	2935 (s)	2926 (s)
Conjugated carbonyl stretching		1708 (s)	1701 (s)	1699 (w)	1716 (w)	1705 (s)
aromatic rings & (-C=C-C-& –C=C-C=C-) or (β-1, β-β, 5-5, & β-5 inter monomeric lignin connection)		1608(s) and 1502(s)	1604 (s) and 1490 (w)	1608(s) and 1508 (s)	1608 (s) and 1508 (s)	1608 (s) and 1514 (s)
C-H deformation and aromatic ring vibration		1458(s)	1456 (s)	1456 (s)	1458 (s)	1454 (s)
Bending vibrations of (-OH) phenolic bonds		---	----	----	1384 (m)	1384 (w)
Aromatic ether aryl (4-O-5 inter monomeric lignin connection)		1273 (s) and 1219 (s)	---	1274 (s) and 1221(m)	1273 (m) and 1217(m)	1278 (s) and 1219 (s)
Cyclic ether large ring stretching (DODO inter monomeric lignin connection)		1111 (s)	1105 (s) and 1024 (w)	1114 (s)	1111 (s)	1109 (s) and 1033 (w)
Alkyl substituted ether (O - CH_3 or O – CH_2 stretch)		1165 (w)	-----	-----	1165 (m)	----
Vinyl ether (in phase C- O - C stretch)		848(w)	-----	852 (m)	852(m)	----

Abbreviations used in the table; w, feeble, m, moderate, s, strong.

UV – Vis. Characterization.

Here, 5 testers of Klason Lignin of investigated Iraqi Phoenix date palm fronds have been dissolved in ethanol (80%) to formulate 5 solutions of 100 mg / L concentration with 10 ml volumetric flasks. UV/Vis. scanning bands are investigated. The spectral details are clarified in Table 3 that λ – maxes and absorbencies based on Figures (8 – 12). Dual regions of peaks have been acquired in each Klason Lignin sample. The 1st one has supreme λ within (228 – 231) nm range at small wavelengths, and the 2nd possess maximum λ within (257 – 274) nm range at long wavelengths. The presence of these characteristic peaks in the lignin bands were based on aromatic ring of not-condensed phenolic clusters in lignin (López M, Huerta-Pujol O, Martínez-Farré FX, Soliva M., 2010) for extreme λ magnitudes at small wavelengths, and Cyclic ether huge ring (DODO inter monomeric lignin connection) regarding supreme λ magnitudes at lengthy wavelengths. The bottommost absorbing at small wavelength of 228 nm is for Gibgab lignin signposts that the non-condensed phenolic clusters (aromatic ring) in lignin have a lowermost presence probability. However, the extreme absorbing at small wavelength (231 nm) is concerning Mtawag lignin, specifies that aromatic ring of not-condensed phenolic clusters in lignin possess a greater existence likelihood. Correspondingly, the lowermost absorbing at long wavelength of 274 nm is concerning Gibgab lignin specifies that Cyclic ether huge ring (DODO inter monomeric lignin connection) possesses the lowermost presence likelihood, whereas an utmost absorbing at lengthy wavelength of 270 nm is concerning Mtawag lignin specifies that Cyclic ether large ring (DODO inter monomeric lignin connection) possess a greater presence likelihood. These clarifications are detailed with the FT–IR band as illustrated in Table 2.

Table 5: UV- absorbance of investigated Iraqi Phoenix date palm pruning woods Lignin**.**

Klason Lignin	Small wavelengths (nm).	Absorbance (A)	Long wavelengths (nm)	Absorbance (A)
Phoenix - Gibgab	228	0.961	274	0.397
Phoenix- Bint- Swelih	228	1.623	257	1.176
Phoenix – Mtawag	231	2.620	270	1.322
Phoenix – Ohm- Al-Blales	231	2.553	271	1.307
Phoenix- Hillawi	229	1.773	270	0.843

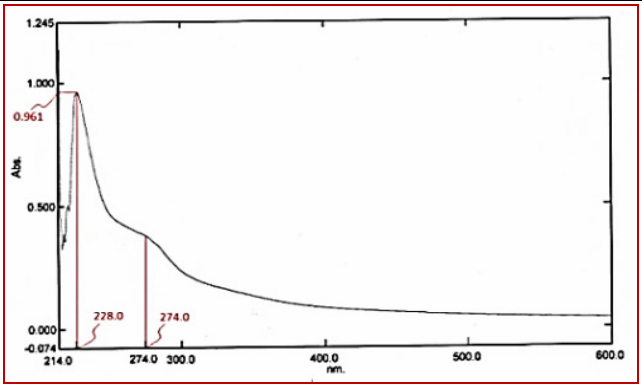


Fig. 8: Lignin UV/Vis. band of Phoenix – Gibgab Pruning

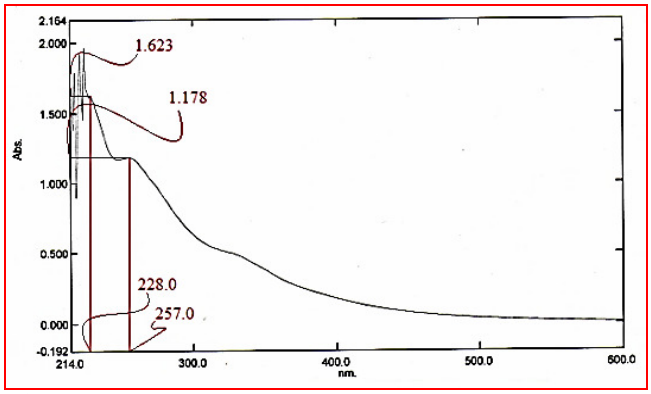


Fig. 9: Lignin UV/Vis. band of Phoenix – Bent Sweleh Pruning

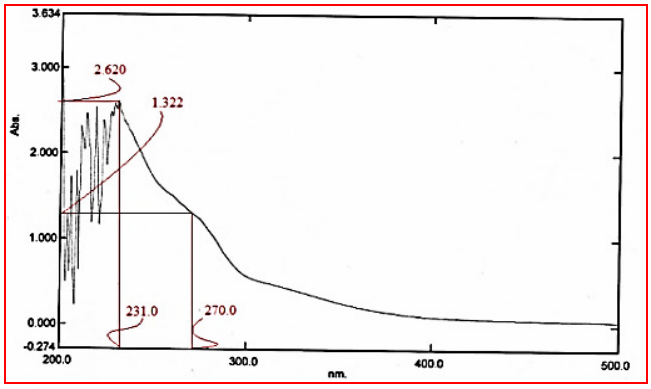


Fig. 10: Lignin UV/Vis. band of Phoenix Mtawak Pruning

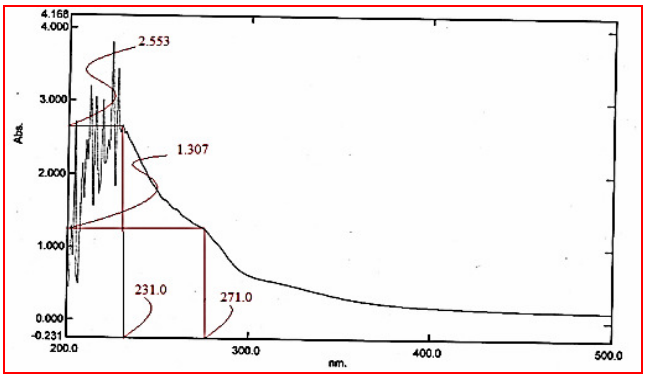


Fig. 11: Lignin UV/Vis. band of Phoenix – Ohm Alblaliz Pruning

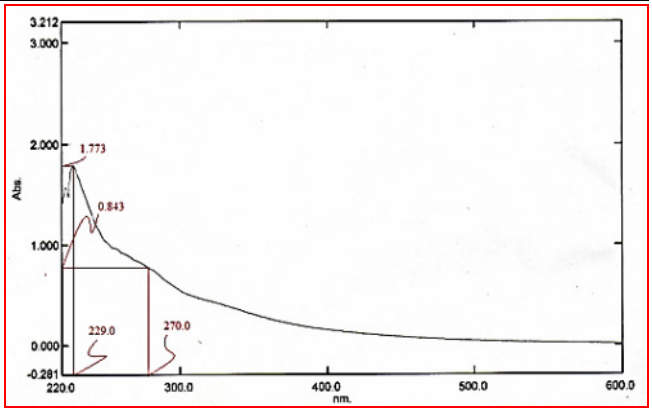


Fig. 12: Lignin UV/Vis. band of Phoenix – Hillawi Pruning

Conclusions

Dissimilar investigated Phoenix date palm fronds wood has been discovered. Maximum lignin percentage of was in Bint-Swelih frond wood, and bottommost lignin percent of has been in Gibgab frond wood. FT–IR spectrums have illustrated that (-OH) phenolic cluster disappear in each tester, excluding Ohm-Al-Blales lignin that have moderate intensity peak, and Hillawi lignin that have feeble intensity peak as a result of the likelihood of free fundamental transitional creation from (-OH) phenolic cluster site. The explanations of UV–Vis. Spectrum show the congruence with the FT–IR spectrum. And this is clear evidence of the success of our research.

Acknowledgments

We would like to thank all people who supported us in this study. Additionally, we have shown a huge gratitude to Head of Faculty of Education Ibn al-Haitham, Chemistry, department for their truthful cooperation in this study.

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