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Synthesis and Characterization of Epoxidized *Thevetia Peruviana* Seed Oil

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ABSTRACT

The seed oil of *Thevetia peruviana* was extracted using soxhlet extraction method with n-hexane. The physicochemical parameters of the extracted oil were determined using standard analytical methods. The extracted oil was epoxidized using peracid generated in situ from aqueous hydrogen peroxide (H_2O_2) and glacial acetic acid. The epoxidized oil was analysed for the functional groups present using Fourier Transform Infrared (FTIR) Spectrometer. The physiochemical parameters of *Thevetia peruviana* seed oil showed the following results; acid value (3.86 mg KOH/g), iodine value (92.5 Wij's), peroxide value (30.0 meq/kg), kinetic viscosity (1.7cp) and saponification value (121.76 mgKOH/g) while the epoxidized oil has acid value (0.49 mg KOH/g), iodine value (68.10 Wij's), peroxide value (7.99 meq/kg), kinetic viscosity (5.57cp) and saponification value (156.1 mgKOH/g). The FTIR results showed that both unepoxidised and epoxidized oils showed the following functional groups OH at wavelengths 3469.50 cm^{-1}, 3468.72 cm^{-1} and 3467.75 cm^{-1}; CH at 2917.75 cm^{-1}, 2922.47 cm^{-1} and 2924.61 cm^{-1}; CH_2 at 2852.39 cm^{-1}, 2852.81 cm^{-1} and 2853.68 cm^{-1}; C=O at 2679.32 cm^{-1}, 2679.41 cm^{-1} and 2673.30 cm^{-1}; C=C at 1656.14 cm^{-1}, 1654.55 cm^{-1} and 1655.5 cm^{-1} while the C≡C at wavelength 2030.69 cm^{-1} that was identified in the unepoxidised oil was found to be absent in the epoxidised oil and a peak indicating epoxyl group was identified in the epoxidized oil. The percentage conversion of oxirane was determined to be 83.5%. This shows that epoxides were effectively formed. The high oil yield and percentage conversion of oxirane makes *Thevetia peruviana* a good feedstock for production of industrial intermediates

ARTICLE DETAILS

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1.1 INTRODUCTION

Plant oils also called vegetable oils form part of the family of chemical compounds known as fats and lipids. This class of compounds is made up of fatty acids and triesters of glycerol which are commonly called triglycerides. Fats of all types have been used in many fields, such as foods, fuels, lubricants and raw materials for other chemicals due to their unique chemical structures and physical properties (Wallace, 1998). Vegetable oils are used as a condiment or constituent in many manufactured products such as skin products, candles, soaps, biodegradable hydraulic fluid and lubricant.

2.1 THEVETIA PERUVIANA

Thevetia peruviana is a plant also known as yellow oleander, lucky nut, bush milk, orange oleander or kolkaphul. In Nigeria, *T. peruviana* has been grown for over fifty years as an ornamental plant in homes, schools and churches (Ibiyemi *et al.*, 2002), flowers and fruits all the year round, providing a steady supply of seeds from fruits of between 400 – 800 per annum depending on the rainfall pattern and plant age (Balusamy and Manrappan, 2007), each of the fruits contains between one to four seeds of oil content 60 to 65 % in its kernel (Ibiyemi *et al.,* 2002).

Thevetia peruviana seed contains more than 62% oil which is not edible. Therefore industrial and academic research in oleochemistry concentrate more on the hydrocarbon chain of fatty acids, especially on the carbon-carbon double bond of the unsaturated fatty acids and the major reactions on the unsaturation applied in industry are hydrogenation and epoxidation. The formed epoxide is an intermediate that can be converted to a variety of products, hence the essence for synthesis and characterization of the epoxidized oil.

2.2 EPOXIDATION

Epoxidation of vegetable oil

The double bonds in the vegetable oils are used as reactive sites in coatings and they can also be functionalized by epoxidation. The epoxidized vegetable oil has been of great importance in the past few years. Epoxidized vegetable oil contains oxirane rings or epoxide groups. The term epoxide can be defined as cyclic ethers which consist of three elements in the epoxide ring. The general process for the synthesis of the epoxide groups is known as an epoxidation reaction wherein an alkene is reacted with an organic peroxy acid (Dinda *et al.,* 2008).

In-situ epoxidation using hydrogen peroxide as oxygen donar and acetic or formic acid as the peroxygen carrier has achieved commercial importance (Latourette *et al.,* 2006). With hydrogen peroxide and acetic acid, however, acid catalysts, such as sulfuric acid or strong cation exchange resins, are needed to speed up peracid formation, whereas performic acid formation requires no strong acid. The reaction is always carried out under isothermal condition (James *et al.,* 2010).

3.1 MATERIALS AND METHODS

- **Apparatus used**

Retort stand, Heating mantle, Soxhlet apparatus, Analytical weighing balance, filter paper, Thread, Blending machine, Oven, Beakers, cotton wool, Razor Blade, Tap, Separation funnel, Thermometer, Magnetic stirrer and plate, Spatula, Hand gloves, Litmus paper.

- **Reagents used**

Distilled water, n-Hexane, Glacial acetic acid, Hydrogen peroxide, Toluene, Benzene, Glacial acetic acid, Hydrobromic acid 48% solution and Crystal violet (the solvents used were analytical grade).

3.2 SAMPLE COLLECTION

Thevetia peruviana fruits were harvested from *thevetia* plantations grown at a residence along Housing Road Ado-Ekiti, Ekiti State, Nigeria. Stainless knife was used to manually decorticate the harvested *thevetia* fruits to reveal the kernels. Thevetia kernel was dried under the sun for 6 hours continuous to ease the removal of the seeds from them. After the seed was removed from the kernels, they were milled into powdered form using a blending machine and stored for extraction.

3.3 EXTRACTION OF OIL

60g of the ground seed sample was wrapped in a filter paper and put into a soxhlet extractor. A 250ml of n-hexane was poured into a 500 ml round bottom flask fixed to the end of the apparatus and a condenser was tightly fixed at the other end of the extractor. The temperature was set to 60ºC for 3hours. As the boiler warmed up, the solvent turned into pure vapour that ascended through a by-pass and reached the upper section of the Soxhlet container (thimble) where the sample to extract was contained. In the condenser, the vapours condensed and drip into the sample-containing thimble. The liquid with the extracted material flowed back into the boiler through the siphon when it reached the same height as the siphon's top. The mixture of the extracted oil and solvent was collected, separated and purified to get solvent-free oil. The above procedure was repeated several times until a reasonable quantity of the oil was obtained and the percentage oil yield was calculated.

3.4 EPOXIDATION OF EXTRACTED OIL (1:0.5:1)

10g of *Thevetia peruviana* seed oil was weighed using analytical weighing balance and dissolved in 100ml of toluene in a beaker. The beaker and the content was placed on a magnetic plate and the stirrer place in the oil. 1.0g of glacial acetic acid was added while stirring continued at temperature between 10-15ºC to homogenise.

5ml of 30% hydrogen peroxide (H_2O_2) was measured, added drop wisely and slowly over a period of 1 hour at temperature between 10-15ºC. After the addition of H_2O_2, the reaction was allowed to continue at room temperature for 24 hours with rapid stirring.

The reaction mixture was poured into a vacuum flask to settle and the aqueous layer was drained off. The organic layer was washed twice repeatedly with warm water and then with cold water. The cold water washing continued till the layer was neutral to litmus paper.

4.1 PHYSIOCHEMICAL PROPERTIES

Result of the physiochemical parameters of the unepoxidised and epoxidized *Thevetia peruviana* seed oils are presented in table 4.1 below.

Table 4.1. Physicochemical properties of unepoxidised and epoxidized *T. peruviana* oil

Properties	TPO	ETPO
Oil yield %	64.33	--
Iodine value (mg KOH/g)	92.5	68.10
Acid value (mg KOH/g)	3.86	0.49
Saponification value (mg KOH/g)	121.76	156.10
Peroxide value (meq/kg)	30.0	7.99
Kinetic viscocity (cp) @ 35ºC	1.7	5.57
Colour	Golden yellow	Whitish yellow

NB: TPO = *Thevetia peruviana* oil, ETPO = Epoxidised *Thevetia peruviana* oil

- **Percentage Oil yield**

The percentage oil yield of Thevetia seed oil was found to be 64.33%. The oil contents of the Yellow Oleander seed (64.33%) obtained in this work compare favourably with the oil yields of yellow oleander seeds (48.8%-60.0%) reported by Dhoot *et al.* (2011). This value also compare favourably with those from other oil bearing plants such as Jatropha kernel (52.4%-56.5 %) as reported by Emil *et al.* (2009). This value falls within the acceptable range of the percentage oil content (52-65 %) of *Thevetia peruviana* seed reported by Ibiyemi *et al.* (2002). However, the oil yields are higher than those of *Azadirachta indica* (44.5%), *Pangamia pinnata* (33%) and *Ziziphus mauritiana* (34%) (Azam *et al.*, 2005). The result of the oil yield showed that *Thevetia peruviana* plant can be classified as oil seed and thus, can used commercially for production of biodiesel (Emil *et al.*, 2009).

- **Iodine value**

The iodine value was obtained using the Wij's method. The iodine value was determined experimentally to be 68.10 mg KOH/g in EPTO while 92.5 mg KOH/g in TPO. The iodine value of TPO is higher than that of ETPO because it contains higher degree of unsaturation that was reduced due to the substitution of carbon to carbon double bonds by oxirane group in ETPO functional groups. (Dinda *et al.*, 2008). The decrease confirms the conversion of C=C double bonds to oxirane ring.

- **Saponification value**

The saponification value was found to increase from 121.76 mg KOH/g in TPO to 156.10 mg KOH/g in ETPO. The saponification value of ETPO is higher than that TPO because of high degree reduction in unsaturation nature of the TPO oil by epoxidation process (Okieimen *et al.*, 2005).

- **Acid value**

Acid value represents free fatty acid content due to enzymatic activity and is usually infective of spoilage. The acid value was decreased from 3.86 mg KOH/g in TPO to 0.49 mg KOH/g in ETPO and peroxide value from 30.0 mg KOH/g to 7.99 meq/g. This reduction indicates that the modified oil can be used in the lubricant world as a precursor. The value was found in the range of the accepted acid value for lubricating oils 0.1 – 10 mg KOH/g. The acid value of the epoxidized *Thevetia peruviana* seed oil obtained in this work is favourable compare with that (2.7 mg KOH/g) reported by Chindo *et al.* (2013).

- **Kinetic viscosity**

A drastic increase in kinetic viscosity was observed. This of the epoxidized oil when used in poly urethane formation will decrease its density, increase the mechanical properties and improve its thermal stability as reported by Fukai *et al.* (2021).

4.2 FOURIER TRANSFORM INFRARED SPECTROMETER (FTIR)

The FT-IR spectra of unepoxidised and epoxidized *T. peruviana* oil (8hrs and 24hrs) are shown in Fig. 4.1, 4.2 and 4.3 respectively. The table for the functional groups is presented in table 4.2.

Table 4.2. Summary of significant bands appearing in Figure 4.1, 4.2 and 4.3.

TPO		**ETPO (8hrs)**		**ETPO (24hrs)**	
Wavenumber (cm^{-1})	**Bond**	**Wavenumber (cm^{-1})**	**Bond**	**Wavenumber (cm^{-1})**	**Bond**
3469.50	OH	3468.72	OH	3467.75	OH
3006.11	C=C-H	3005.91	C=C-H	3005.41	C=C-H
2917.75	C-H	2922.47	C-H	2924.61	C-H
2852.39	CH_2	2852.81	CH_2	2853.68	CH_2
2679.32	H-C=O	2729.41	H-C=O	2673.30	H-C=O
2030.69	C≡C				
1746.63	C=O	1746.71	C=O	1740.35	C=O
1656.14	C=C	1654.55	C=C	1655.5	C=C
1455.68	CH_2	1455.49	CH_2	1464.94	CH_2
1117.86, 1162.08, 1238.85	C=C-C-O	1117.8, 1162.7, 1238.24	C=C-C-O	1117.87, 1163.6, 1238.14	C=C-C-O
1032.43	C-O	1032.09	C-O	1034.60	C-O
		823	C-O-C		

NB: TPO = *Thevetia peruviana* oil, ETPO = Epoxidised *Thevetia peruviana* oil

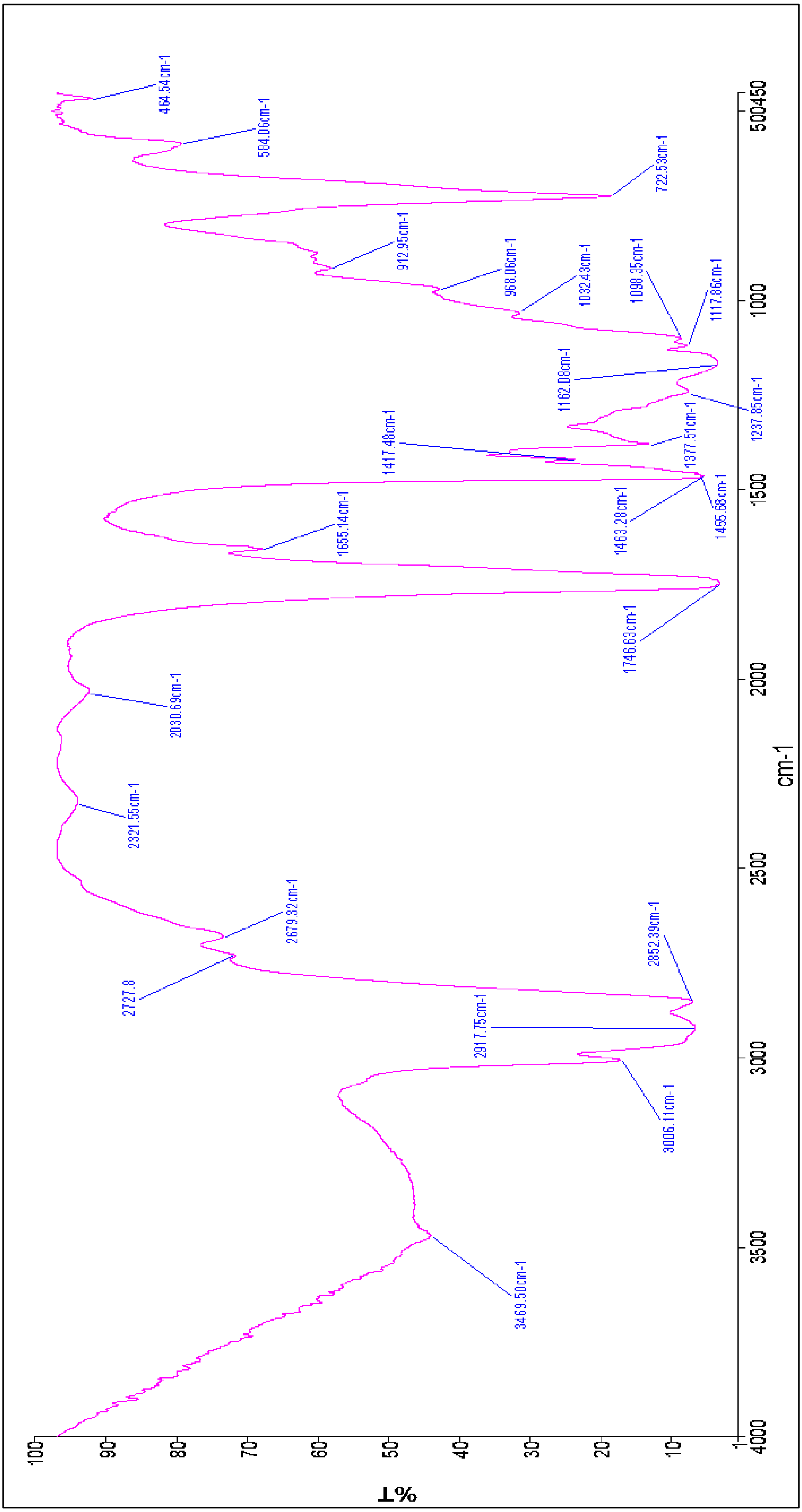

Figure 4.1: The FT-IR spectra of unepoxidised T. peruviana oil

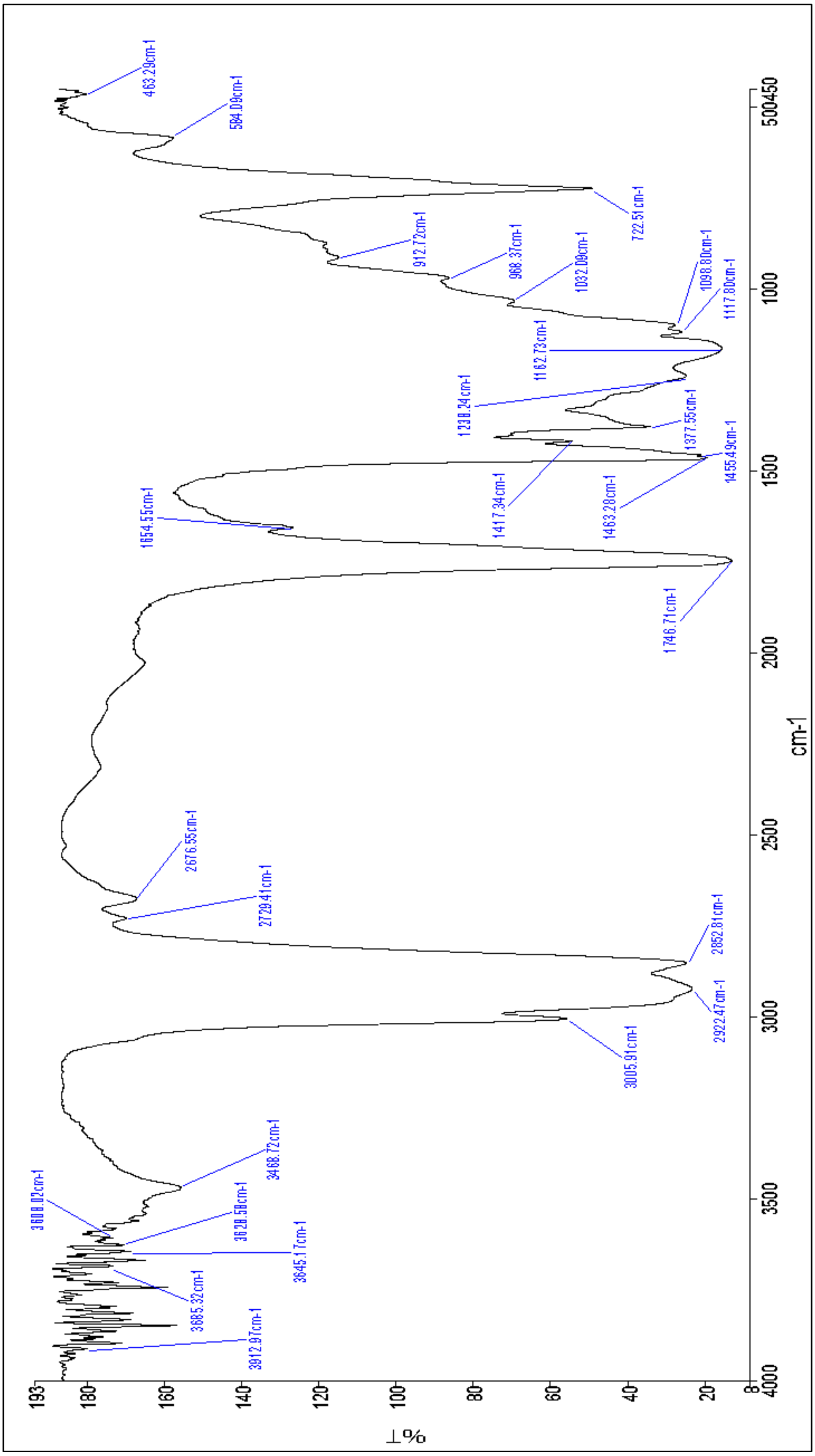

Fig. 4.2. FT-IR spectrum of 8hrs epoxidized *Thevetia peruviana* oil

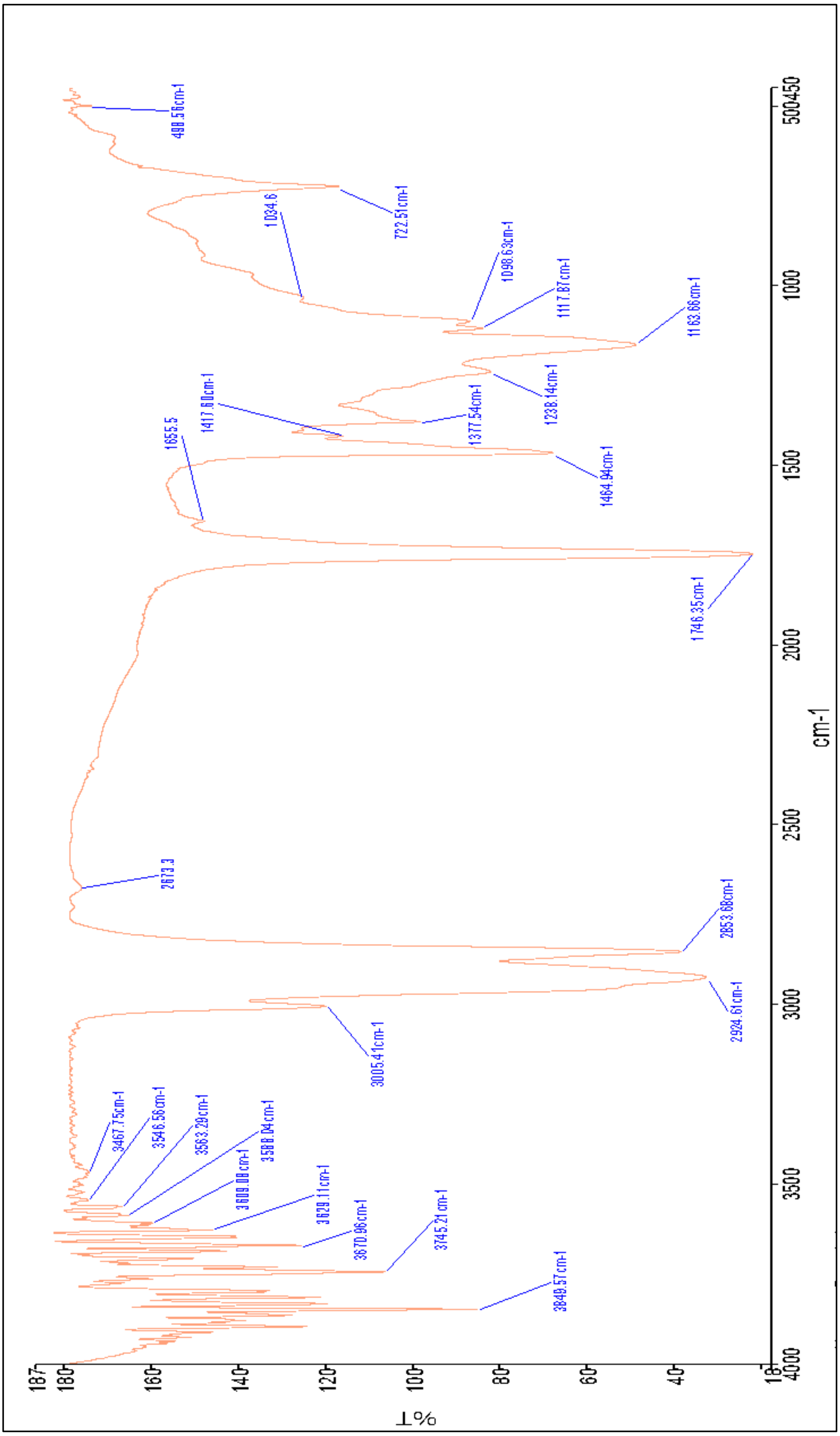

Fig. 4.3: FT-IR spectrum of 24hrs epoxidized Thevetia peruviana oil

Interpretation

The FT-IR spectra of unepoxidized and epoxidized *T. peruviana* oil (8hrs and 24hrs) are shown in Fig. 4.1, 4.2 and 4.3 respectively. The table for the functional groups is presented in table 4.2.

The vibration at 3469.50 cm^{-1}, 3468.72 cm^{-1} and 3467.75 cm^{-1} are assigned to OH stretching. It is likely that the OH group appearing at this band is due to the presence of a percentage of H_2O in the sample. It is commonly accepted (Albuquerque *et al*., 2003) that the vibrations at 3005.91 cm^{-1} , 3006.11 cm^{-1} and 3005.41 cm^{-1} in fig. 4.1, fig. 4.2 and fig. 4.3 are the same for most vegetable oils and is due to the CH stretching related to C=C-H bonding. This band is an important consideration in this research as it is this double bond that is consumed to produce an epoxy group. A successful epoxidation reaction is considered to be one that consumes all of this peak, suggesting that the maximum number of epoxy groups may have formed. The next three bands are assigned to the C-H stretching of methyl (CH_3) and methylene (CH_2) groups. Asymmetric stretching of a CH_3 group is responsible for the vibration at 2922.47 cm^{-1}, though it produces only a minor peak. Two highly pronounced bands follow at vibrations 2852.8cm^{-1} and 2729.41 cm^{-1} are common to most triglyceride oil spectrums. They are the result of CH_2 asymmetric and symmetric stretching vibrations, respectively.

Noticeable bands at vibrations 2679.32 cm^{-1}, 2729.41 cm^{-1} and 2673.30 cm^{-1} in fig. 4.1, 4.2 and 4.3 respectively indicate C=O stretching vibration which is attributed to the presence of methyl esters and 2030.69 cm^{-1} in the base oil spectrum (Fig. 4.1) corresponds to alkyne group, C ≡ C stretch. This band disappears in the epoxidised spectra which indicates the consumption of unsaturated bonds to produce epoxides.

Strong bands appear at vibrations 1746.63 cm^{-1}, 1746.71 cm^{-1} and 1740.35 cm^{-1} correspond to the C=O stretching vibration of the carboxylic groups. This group is present in all fatty acid chains and occurs adjacent to where the fatty acid chain joins to the glycerol molecule. The epoxidation process has little effect on the absorbance of the carboxylic groups, for that reason this band will remain virtually unchanged for the vegetable oil and its epoxidised counterpart. This is an advantage as it allows the spectrum of the epoxidised vegetable oil to be normalised against the spectrum of the original vegetable oil. To the right of this band in fig. 4.1 appears a very weak band at vibration 1654.55 cm^{-1}. This band is assigned to a C=C stretching vibration. Researchers verify this as being correct as this band doesn't appear on spectrum of saturated vegetable oils, in which the C=C bond doesn't occur (Albuquerque *et al*., 2003). Examining the spectrum of epoxidised vegetable oils it was observed the band has diminished, there's a distinct possibility that the epoxidation reaction was successful. A well pronounced band at 1465 cm^{-1} is assigned to the CH_2 scissors deformation vibration. The CH_2 group is common in the triglyceride molecule, though there is no information found relating to whether it is specific to the occurrence of this group in the glycerol or fatty acid segments of the triglyceride molecule, or both. The CH_2 band stay relatively unaffected by the epoxidation reaction.

A prominent band occurs at vibration 1163 cm^{-1} and very sharp in fig. 4.3 (24hrs epoxidized oil spectrum). On either side are two weaker bands at vibrations 1238 cm^{-1} and 1117.8 cm^{-1}, before and after respectively. This profile of bands is assigned to the C=C-C-O stretching vibration. They appear weaker in the spectrum of epoxidised samples (Fig. 4.2 and Fig. 4.3) compared to the spectrum of the base vegetable oil, due to the consumption of the double bonds. There was significant difference in this band between both the base and epoxidised sample spectra.

A significant band appearing at vibration 722.5 cm^{-1} is assigned to the CH_2 rocking mode. Another band of great importance which doesn't appear in base spectrum occurs at vibration 823 cm^{-1} but disappear in fig. 4.2 (the 8hrs spectrum). This band is assigned to the C-O-C epoxy group and is not well noticed in fig. 4.3, the spectrum of base vegetable oil. The disappearance of this band in the 24hrs spectrum can be concluded that after some hours, the epoxides deform though its occurrence is evident in the spectrum of epoxidised samples. A band was noticed at vibration 584.06cm^{-1} in the base spectrum which is assigned to C-Br stretching but not noticed in the epoxidized spectra. This can be as a result of reagent (KBr) used during the analysis.

4.3 OXIRANE OXYGEN CONTENT

The theoretical oxirane oxygen content is estimated from the Equation below, where IVo is the triglyceride iodine value of the VO, Ai (126.9) is the atomic mass of iodine and Ao (16.0) is the atomic mass of oxygen.

$$\boxed{OO_t = \left[\frac{\left(\frac{IV_0}{2\cdot A_i}\right)}{100+\left(\frac{IV_0}{2\cdot A_i}\right)\cdot A_0}\right]\times A_0\times 100}$$

Oxirane oxygen by theoretical (oo_t) =

$$\frac{\frac{93.50}{2\,x\,126.9}}{100+\frac{93.50}{2\,x\,126.9}x16}\,x16\,x100$$

$$= 5.57$$

Oxirane oxygen by experiment (OO_e) $= \frac{1.6\,x\,N\,x\,V}{W}$

$$= \frac{1.6\,x\,0.1187\,x\,9.8}{0.4}$$

$$= 4.65$$

$$\%\ \text{conversion} = \frac{OO_e}{OO_t}\ x\ 100\%$$

$$= \frac{4.66}{5.57}\,x\,100$$

$$= 83.5\%$$

The oxirane oxygen conversion was found to be 83.5%. This shows that 83.5% of oxygen was introduced into the double bond ring to form the epoxyl group during epoxidation. The higher the oxirane oxygen conversion, the higher the percentage epoxidation and vice versa.

CONCLUSION

This study shows the possibility of obtaining industrial precursors from ornamental garden plant *T. peruviana* oil. It can potentially be utilized as a feedstock of large scale production based on the yield and its physiochemical properties. Therefore, it can reduce the dependency on using edible oil feedstock. This renewable material and high sustainability makes the *Thevetia peruviana* oil a suitable natural building block for the preparation of useful bio-polymer materials serving as alternative to the use of petroleum resource in chemical and allied industries. This results in a maximum relative conversion to oxirane of 83.5%. It can also be concluded that epoxides are formed from 8hrs but get deformed when reaction is left to continue for longer hours.

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