Pertanika J. Sci. & Technol. 27 (4): 2221 - 2243 (2019)

PERTANIKA JOURNALS

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

Fatty Acid Profile and Production of Fatliquor from *Canarium schweinfurthii* Mesocarp Oil

Adachukwu Nwaka Nkwor[1]*, Pius Oziri Ukoha[2], William Robert Wise[3], Njemuwa Njoku Nwaji[1] and Karl Flowers[3]

[1]Department of Chemistry/Biochemistry/Molecular Biology, Alex Ekwueme Federal University Ndufu-Alike Ikwo, P.M.B 1010, Abakaliki, Ebonyi State, Nigeria
[2]Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka 410001, Enugu State, Nigeria
[3]Institute for Creative Leather Technologies, The University of Northampton, Park Campus, Boughton Green Road, NN2 7AL, Northampton, United Kingdom

ABSTRACT

Fatty acid profile of *Canarium schweinfurthii* mesocarp oil was determined by GC-MS. Sulphonated fatliquor was synthesized from the oil and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and DSC. The fatliquor was applied onto light leather in the processing of leather shoe upper and physical tests carried out on the fixed leather. The sulphonated *C. schweinfurthii* mesocarp oil had good characteristics as a leather fatliquor as shown by the physical and strength properties of the fatliquored leather. In addition, a significantly opened up structure of the leather treated with the prepared sulphonated oil was observed as indicated from the Scanning Electron Microscopy (SEM) images. The features of the processed trial leathers were comparable with similar leather made with commercially available fatliquor.

Keywords: Canarium schweinfurthii, characterisation, fatliquor, leather, oil, sulphonated

ARTICLE INFO

Article history:
Received: 31 January 2019
Accepted: 11 July 2019
Published: 21 October 2019

E-mail addresses:
adannkwor@yahoo.com; adachukwu.nkwor@funai.edu.ng (Adachukwu Nwaka Nkwor)
pius.ukoha@unn.edu.ng (Pius Oziri Ukoha)
will.wise@northampton.ac.uk (William Robert Wise)
njemuwa2005@yahoo.com (Njemuwa Njoku Nwaji)
plugsly@gmail.com (Karl Flowers)
* Corresponding author

INTRODUCTION

In the leather industry, many chemical and mechanical processes are needed to produce finished leather. Fatliquoring process, the last of the wet processing stage in leather manufacturing is a significant step and its importance cannot be overemphasized. When water is removed from chrome tanned leather during the drying stage, cohesion of the fibres takes place and results in leather

ISSN: 0128-7680
e-ISSN: 2231-8526

which is dry, hard, intractable and difficult to work with (Burgess, 1993). The introduction of fatty matter as lubricant in finely dispersed form in a water medium carried out during the fatliquoring process keeps the fibres apart during drying and reduces the frictional forces within the fibre weave, thereby allowing the fibres to slide over one another. Such lubricants include: natural lubricants which are made up of a blend of natural plant / animal oils and emulsifying agents; sulphonated lubricants obtained from a reaction of sulphuric acid and a double bond in an unsaturated fatty acid; sulphited lubricants, produced when highly oxidised fatty raw materials react with sodium bisulphite to give oxy-sulphonic acids. Other lubricants include synthetic lubricants, produced when various kinds of chemical modifications such as sulpho-chlorination are catalytically carried out on paraffins (Daniels, 2001).

These lubricants, known as fatliquors, also improve the mechanical/strength properties of leather such as tensile strength, pliability, soft handle and tear load (Heidemann, 1993). They also aid resistance to acid attack and help in preventing the ugly appearance of chrome tanned leather after drying (Janakiram, 2007).

The property obtained in each vegetable-based fatliquor differs from the other and it depends on the properties found in the vegetable oil used (Janakiram, 2007). *Canarium schweinfurthii*, also known as black date, is an exotic tree which is abundantly available in Sub-Sahara Africa and can be readily found in African countries such as Nigeria, Ethiopia, Sierra-Leone and Sudan (Evans, 2004). The tree, which grows in the wild in Africa, produces oval- shaped fruits. These fruits have edible mesocarps which are eaten as supplement to diet.

In this study, oil from the mesocarp of *Canarium schweinfurthii* was sulphonated and used as a leather lubricant for chrome tanned goatskins. After the characterisation of the oil and the sulphonated fatliquor had been produced, the fatliquoring ability was assessed by comparing it with an imported fatliquor commonly used in Nigerian tanneries.

MATERIALS AND METHODS

Sample Preparation of Fruits of *C. schweinfurthii*

Mature fruit samples of *C. schweinfurthii* were obtained from where they grow wildly at Onueke, in Ebonyi State, Nigeria. The samples were identified in the Herbarium Unit, Department of Biological Sciences, Ahmadu Bello University, Zaria, Kaduna State, Nigeria and voucher number 7232 was assigned to it. The mesocarp was manually peeled from the fruits to separate it from the kernel and dried in the oven (40^{o}C) for five days until it became crispy, thus obtaining minimum moisture content (Abayeh et al., 1999). The dried mesocarps were coarsely ground (approximately 2 mm) using the Corona hand kitchen grinder, before extraction. The extraction of the oil from the seeds was carried out in a soxhlet apparatus using n-hexane as a solvent.

Physical and Chemical Characteristics

Both the sulphonated and unsulphonated oils were analyzed for their physical and chemical properties according to the American Oil Chemists Society Methods (Firestone, 1998).

Fatty Acid Composition

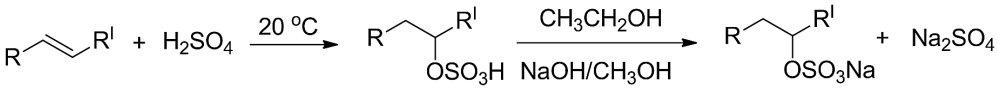
Fatty-acid composition of *Canarium schweinfurthii* oil, CSO was determined using its methyl ester prepared with the method described by Adewuyi et al., (2014) on an Agilent19091S-433HP-5MS gas chromatograph attached to a mass spectrometer. The injection and detection temperatures were 280 and 300°C respectively. Helium was used as the carrier gas at a flow rate of 20 ml/min. The area percentages were recorded with a standard Chemstation Data system. For the mass spectrometry, an ACQ mode scanner (with scan range of 15-500 amu and voltage of 2094) was used and the mass spectra were compared with the NIST11 mass spectral library.

Sulphonation Process

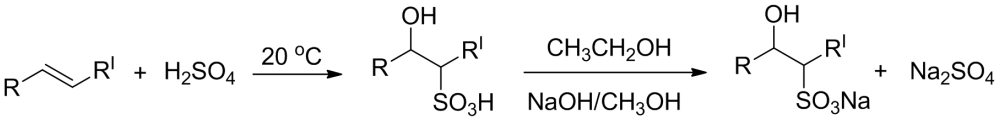
Concentrated sulphuric acid (45 ml) was added dropwise into 150 g of *C. schweinfurthii* oil (with constant stirring at 20°C for 2 h). The crude mass was dissolved in 450 ml of ethanol, and neutralised using 15% NaOH (solubilised in methanol). The salts were filtered off under vacuum. The solvent was removed and recovered using a rotary evaporator (Steik, 1943). The resulting sulphonated product was ready for use as a leather fatliquor.

This reaction of unsaturated oils with sulphuric acid is additional.

Sulphonation process:



Scheme 1. Sulphonation of *C. schweinfurthii* oil to produce sulphonated (Sulphated) oil



Scheme 2. Side by side reaction of the sulphonation of *C. schweinfurthii* oil

Melting Point Determination

The thermal behaviour of the *C. schweinfurthii* oil, CSO and Sulphonated *C. schweinfurthii* oil, SCSO was determined using the Mettler DSC 2 Star System in temperature range of -80 to 180ºC.

FT-IR Analysis

The changes in the functional groups of the oils were studied using the FT-IR analysis by FT-IR measurement (600-4000 cm^{-1}), normal resolution of 4 cm^{-1} using a Shimadzu 8400S FT-IR instrument (Shimadzu, Milton Keynes, UK).

NMR Analysis

^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra of both CSO and SCSO were acquired on a Bruker Biospin AV500 – 5mm BBO probe with Z axis gradient, TOPSPIN v 2.1, ^{1}H=500.13 MHz, ^{13}C=125.76 MHz (Brucker, Coventry, UK).

Fatliquoring Process

Wet blue goat skin, shaved at 1.2-1.3 mm, was divided into four quarters such that the sampling positions **(**BS 2418, 2002), were uniformly represented in all the four quarters.

Further treatments on each of the four quarters of the wet blue goat skins labelled NC, PC, A1 and A2 respectively, were simultaneously carried out *(with the aid of four separate tanning drums)* using a conventional shoe upper manufacturing process [fatliquoring process] (ICLT SR15/31, 2015).

A negative control (designated NC) was processed without any fatliquor; a positive control (designated PC) was processed using a commercial sulphated fatliquor, Trupon DXV (Trumpler Gmbh, Worms, Germany). Sample A1 was processed using pure sulphonated *C. schweinfurthii* oil; Sample A2 was processed using a blend of pure sulphonated *C. schweinfurthii* oil and 7.5% raw castor oil. Leather dyeing was omitted in the process to enable the Sudan IV staining test (for identification of fatty substances) be carried out effectively after the leather manufacturing. The fatliquoring process used was illustrated in Table 1.

Strength/Mechanical Properties of Leather

These leather samples: NC, PC, A1 and A2 were conditioned according to (BS 2419, 2002) before mechanical tests were carried out on them. The samples were staked twice using a Cartigliano PAL 160 leather staking machine (Cartigliano, Bassano, Italy) on the lowest setting. The Strength / mechanical properties of leather samples were all determined using; softness (BS 1723, 2015) tensile strength (BS 3376, 2011), elongation at break and tear strength of leather (BS 3377, 2011) and grain strength standards (BS 3379, 2015).

Sudan Stain Test on Leather Samples

Thin sections (50 μm) of the leather samples were cut with a Leica 1850 cryostat microtome (Leica, Wetzler, Germany) (set at -20°C) and used in the Sudan (IV) stain test (Bugby, 1999) for the determination of the extent of penetration of the fatliquors into the leather fibrils.

Scanning Electron Microscopy

Cross sections of experimental and control were examined for changes in fibre structure using Hitachi S-3000N scanning electron microscope, SEM (Hitachi, Maidenhead, UK).

Leather Samples were gold-coated using an Emscope SC 500 gold sputter coater before SEM analysis (Quorom Technologies, Laughton, UK).

Table 1
Fatliquoring process for shoe upper manufacture damp shaved weight: 400 g

Process	% (m/m)	Chemical	T(°C)	Time(min)	Comments
Wet Back	300	Water	30		
	0.2	Surfactant		20	
Drain					
Neutralise	100	Water	35		-
Add	1	Sodium formate		5	
	0.25	Sodium bicarbonate		30	pH = 4.6 Bromo-cresol green cross-section = yellow/ green
Drain					
Wash	200	Water	35	5	
Drain					
Retan/Fat	100	Water	30		
Add	6	Replacement syntan		15	
	4	Vegetable tannin		30	pH = 4.63
	20	Water	35		
	3	Acrylic resin		30	pH = 5.29
Drain					
Wash	200	Water	50	5	
Drain					
Dye/Fat	100	Water	50		
Add	2	Dye		10	Paste if necessary
	6	Fatliquor (1:3)		40	Run longer if needed
Fix add	1	Formic acid (1:10)		20	pH =3.6
Drain, wash X2, horse up					

Source: ICLT SR 15/31

RESULTS AND DISCUSSIONS

Physicochemical Properties

The physicochemical properties of CSO and SCSO are shown in Table 2. The high percentage quantity of oil in *C. schweinfurthii* indicates potential applicability for possible large-scale chemical modification in the synthesis of fatliquor via sulphonation.

The green colour possessed by CSO was not a disadvantage to the final colour of the leather article produced as shown by the 10% solution that had a pale green colour. The specific gravity of the oil is in line with the density of most vegetable oils (Gunstone, 2004). The translucent (not so clear) nature of the 10% solution is an indication of a medium degree of sulphonation (Waite, 1999). This physical observation shows that there was a percentage of SO_3 (anionic emulsifier) incorporated into the sulphonated compound. It should also be noted that SO_3 is the fuel which drives the oil droplets into the leather. It equally ensures a great degree of fixation as they will be attached to the positively charged leather (Covington, 2011).

Fatty Acid Composition

The nature of the fatty acids present in oils affects the ease of sulphonation and the nature of sulphonated product obtained. It can be seen from Table 3 that the ratio of the total unsaturated fatty acids of *C. schweinfurthii* is almost equal to the total saturated fatty acids (1: 0.80). Palmitic acid constitutes more than 94% of the saturated fatty acids while linoleic acid constitutes more than 54% of the unsaturated fatty acid. Oleic acid is also a major unsaturated fatty acid constitutes more than 43% of its content. Details of the GC-MS analysis are shown in Appendix A, B, C, D, E, F, G, H. Since a great percentage of unsaturated fatty acids (55.53%) is found in the oil, the double bonds present in them are readily available for the sulphonation reaction.

Table 2
Physicochemical properties of both CSO and SCSO

Parameter	CSO	SCSO
Percentage Yield (%)	51.32	69.7
Colour	Dark green	Dark green
Odour	Inoffensive	Odourless
Appearance of 10% Solution	-	Translucent
Colour of 10% solution	-	Light green
pH of 10% Solution	-	7.44
Stability of 10% solution	-	Stability> 24hrs
%Ash Content	-	Trace
% SO_3	-	4.05
Specific gravity (at 20°C)	0.948	0.978
Acid Value (mg KOH g^{-1})	11.36	8.25
Free fatty acid (as oleic acid)	5.68	4.13
Iodine value	68	23
Saponification value	196	192

Table 3
Fatty acid profile of CSO

Fatty acid	Percentage composition (%)
Palmitic acid	41.81
Stearic acid	2.66
Saturated fatty acids	44.47
Oleic acid	23.75
Linoleic acid	30.08
Palmitoleic acid	1.70
Unsaturated fatty acids	55.53

Differential Scanning Calorimetry (DSC) Results

It was observed from the DSC results that CSO had a wide melting range of (0.64 to 8.89^{o}C) depicting the various fatty acids (saturated and unsaturated) present in the oil (Table 4). These melting ranges and DSC curves result from the combined effects between fatty acid composition, polymorphism of natural oils and fats, and thermal history (Kaiserberger, 1989). The melting behaviour of the oils CSO and SCSO studied varied due to the different characteristics and compositions of fatty acids present in the triglycerides (Fashina et al., 2008)**.**

The increased melting point observed in the SCSO shows that most of the unsaturated fatty acids have been used up in the sulphonation reaction; leaving behind saturated fatty acids (which have a higher melting point) than unsaturated fatty acids (Berg et al., 2002).

Emulsion Stability Tests

Table 5 shows that 10% fatliquor emulsions of SCSO are generally stable in various salt solutions used in leather manufacturing processes like deliming, pickling and chrome tanning steps. When sulphonated fatliquor which is anionic ionizes in water to release the anionic sulphonate group, these negative ions react electrostatically with the protonated amino group from the basic group of protein in leather and thus fixed up with leather.

This fixation can only be done in an acid medium. The SCSO has a good emulsion stability towards tanning salts, pickle liquor and hard water, but unstable when in contact with formic acid. This instability of the emulsion with formic acid enables the fatliquor to stay in the leather and form bonds that hold it there (Habib & Alshammari, 2014). Table 5, therefore, shows that SCSO can also be used in the retanning and fatliquoring steps.

Table 4
The thermal behaviour of CSO and SCSO

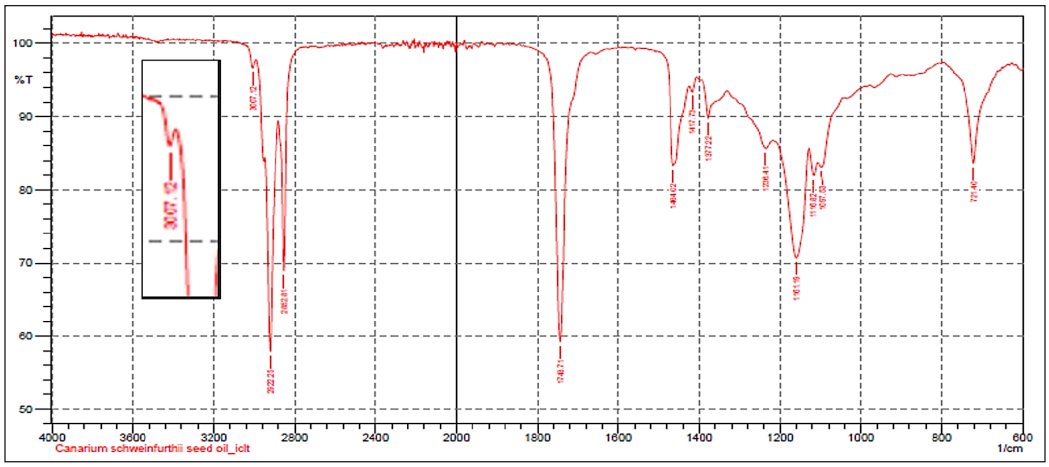
Oil Sample	Onset Temperature (°C)	Peak Temperature (°C)	Endset Temperature (Melting Point) (°C)
CSO	0.64	4.42	8.89
SCSO	7.54	16.5	18.44

Table 5
Stability of 10% fatliquor emulsion of SCSO towards pickle liquor, tan liquor and hard water

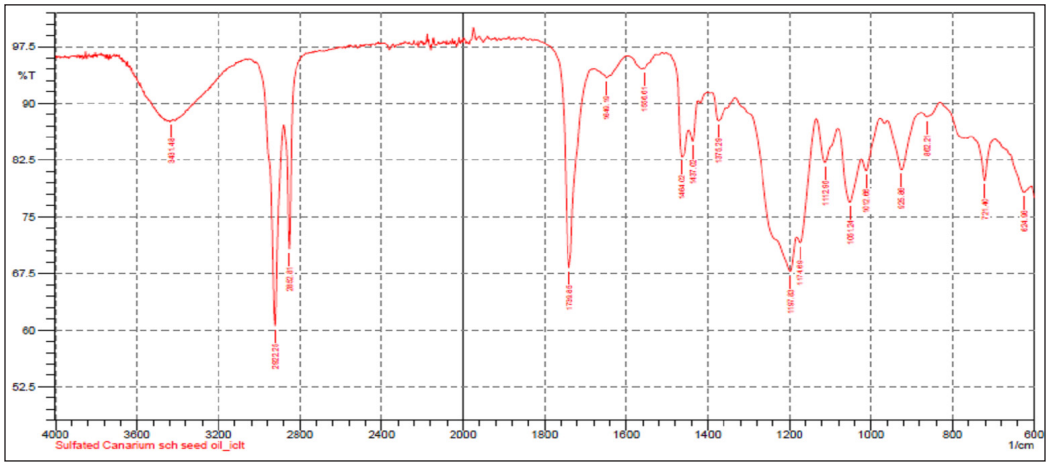
Solution added	Stability Status
5 % Basic chromium sulfate (tan liquor)	Stable
5 % $MgSO_4$ (hard water)	Stable
5 % NaCl (found in pickle liquor)	Stable
5 % Formic acid	Unstable

Fourier Transform Infra-Red (FT-IR) Results

The FT-IR results in Figure 1a and 1b illustrate the IR spectrum of CSO and SCSO. In Figure 1b, the probable attack of H_2SO_4 on the –C=C- to form the sulphonated product was confirmed by the absence of unsaturated C-H stretching peak at 3007.12 cm^{-1} in



(a)



(b)

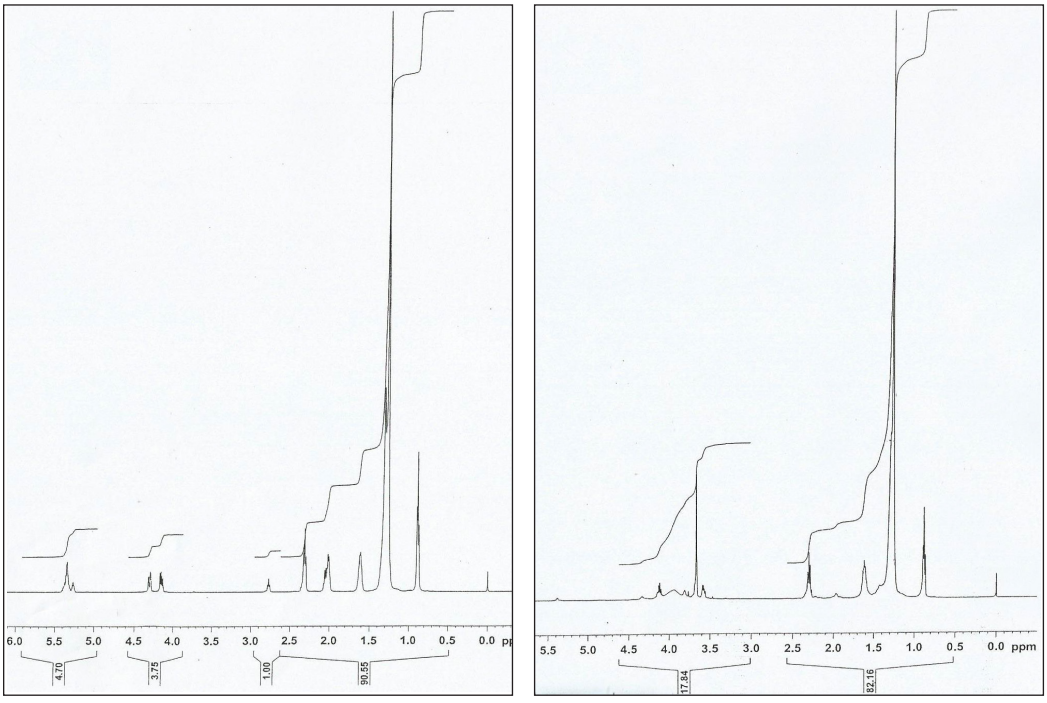
Figure 1. FT-IR spectra of CSO (a) and SCSO (b) (Insert: expanded section of signal showing 3007.12 cm^{-1})

non-conjugated. In addition, the presence of vibrational peak at 1198 cm^{-1} (Figure 1b) corresponds to S=O stretching of sulphonated groups, which is absent in Figure 1a; hence, confirming the formation of sulphonated product.

Other prominent peaks found in both samples are at (2853 cm^{-1}) C-H stretching frequency of alkane; (1744 cm^{-1} (C=O stretching frequency of ester); 1464 cm^{-1} (bending frequency of unsaturated alkene); and 721 cm^{-1} (bending frequency of saturated carbon atom). The OH peak at 3431 cm^{-1} in Figure 1b depicts the traces of alcohol used in the formation of the sulphonated products.

Nuclear Magnetic Resonance (NMR) Spectroscopy Results

The ^{1}H NMR of CSO and SCSO is shown in Figures 2a and 2b respectively, while the ^{13}C NMR spectral diagrams are found in Figures 3a and 3b respectively. The ^{1}H NMR displayed the unsulphonated multiplet olefinic protons attached to C=C double bond at δ 5.29 ppm, integrated into 5 protons. This is expected since these protons are sp^2 hybridized, resulting in deshielded NMR signals due to the influence of the diamagnetic anisotropy of the π system. Sulphation / sulphonation usually lead to the saturation of the double bond. The sp^3 hybridized protons formed are thus expected to be shielded relative to the sp^2 olefinic protons. The newly formed protons (H-C-S and H-C-O) in the SCSO showed signals at



(a) (b)

Figure 2. ^{1}H NMR of CSO (a) and SCSO (b) in deuterated chloroform

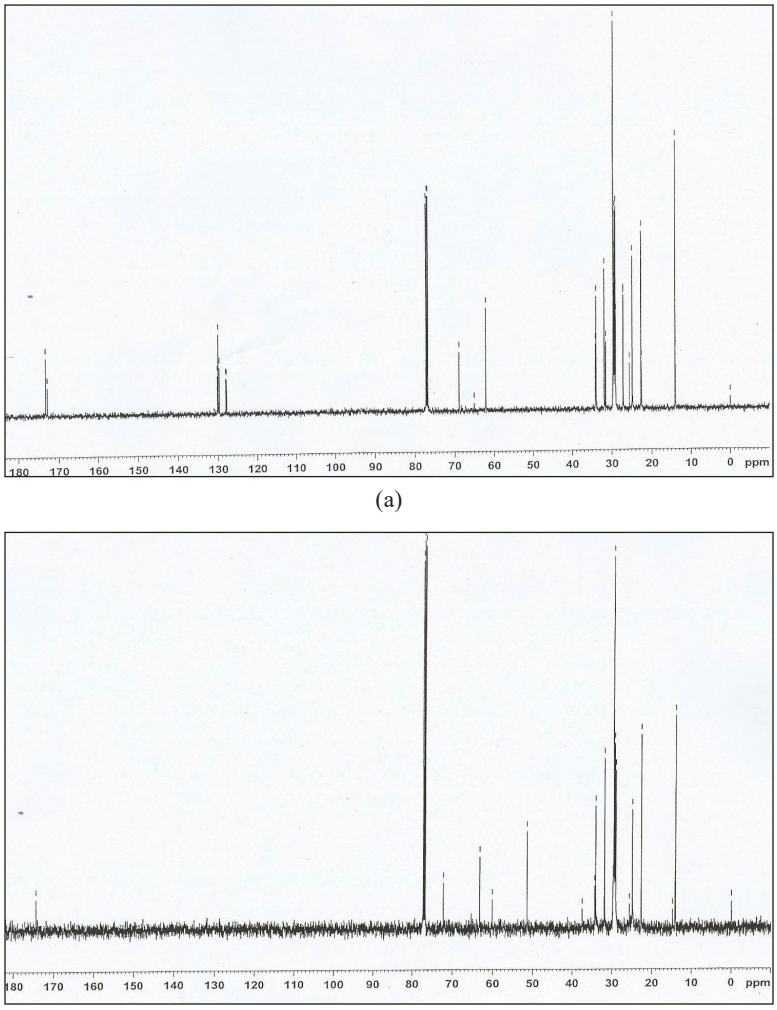


Figure 3. ^{13}C NMR of CSO (a) and SCSO (b) in deuterated chloroform

δ 3.6 and 3.73 ppm. It is important to note that the slight deshielding observed for these protons relative to the rest of the protons in the SCSO is due to the inductive effect of the electronegative sulphur and oxygen atoms. The inductive effect, however, causes less deshielding than diamagnetic anisotropy.

Similar explanation can be used to explain the differences in carbon chemical shifts observed in the ^{13}C NMR for the CSO and SCSO. In the ^{13}C NMR spectra, both the CSO and SCSO have one signal each at around 14.1 ppm (methyl group at the end of the acyl chains in glyceride moiety). It is well separated from other signals and, hence, easily recognized. The same vaIues have been reported in literature (Gunstone, 2004, Okiemen et al., 2005, Sega et al., 2010). In the ^{13}C spectrum, the signals associated with the olefinic

carbons appear highly deshielded at δ 127.09 to 131.85. ppm due to the diamagnetic anisotropic effect of the π system. Upon sulphonation, these signals were absent due to loss of the double bonds. The new signals which appeared at 52 and 72 ppm belong to the sp^3 hybridized carbons (C-S and C-O) formed after the sulphonation reactions. The slightly deshielded position of these signals is also due to the influence of the inductive effect of the electronegative sulphur and oxygen atoms.

Strength Properties of Leather Samples

The strength properties of the leather samples were shown in Figures 4, 5 and also in Table 6. The strength properties of the leather samples were determined both perpendicular and parallel to the backbone and the average results obtained. It is obvious from Figure 4 that despite the other processing techniques which involved conditioning, staking and inclusion of other additives to give leather a soft handle, both the SCSO and its blend with 7.5% castor oil demonstrated a clear improvement on leather without any fatliquor (NC), and was comparable to similar leather made with commercially available fatliquor (PC).

Castor seed oil is normally used in the tanning industry as a source of lubrication because of its humectant property. The strength of grain surface test results is shown in Figure 5. The lowest values for grain crack and grain burst are seen in the negative control (having average grain crack and grain burst strengths of 320 and 335 N respectively). The PC, Pure and Blend, had higher average grain crack of 400, 410 and 405 N respectively, and also grain burst strengths of 450, 415 and 425 N respectively. Proper lubrication of the leather fibres in PC, Pure and Blend brought about the increase in average grain crack and grain burst strength.

Strength properties have been given the greatest consideration in evaluating fatliquored leather because they give an indication of fibre lubricity (Waite, 1999; Burgess, 1993). The sulphonated portion of the oil interacts with the active centres in the collagen molecules of leather fibres and leaves the oil between the fibres. The elongation at break characterizes the softness, flexibility, strength and toughness of the leather matrix (Alexander et al., 1993). It is also evident from the strength properties results that the leather fatliquored using SCSO compared favourably with the commercial fatliquor.

Table 6
Other strength properties results

Properties	NC	PC	PURE	BLEND
Average Tear Load (Double Edge Tear) (N)	354.3	543.4	437.8	496.4
Average Tensile Strength (N/mm^2)	17.38	24.86	22.54	27.07
Average Elongation at Break (%)	28.48	38.04	35.88	37.14

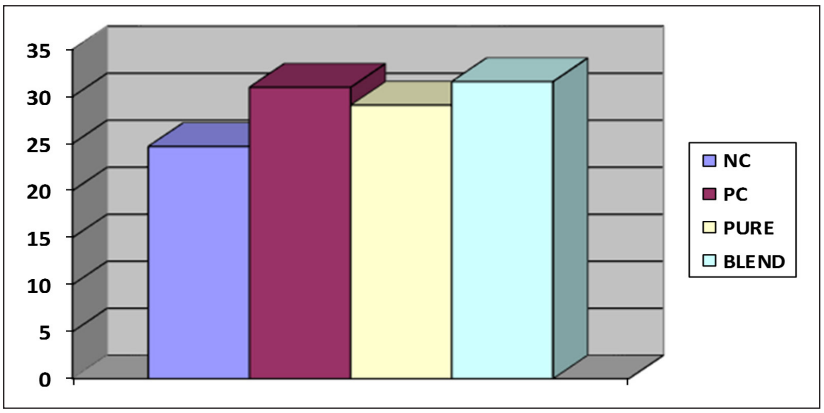


Figure 4. Softness test results

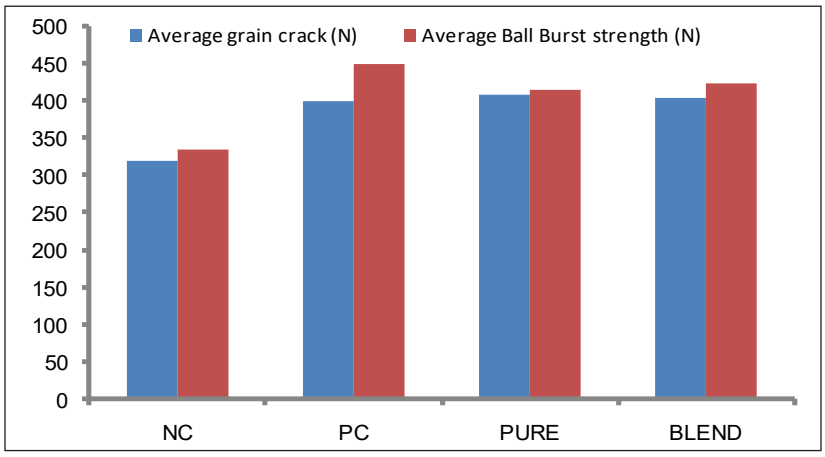


Figure 5. Strength of grain surface of leather

Sudan Stain Test Results

Staining renders visible, components within the section which would not be seen easily. Here, leather fibrils were soaked in Sudan (IV) dyes which were specific for fats and oils and are specially adapted to suit leather microscopy (Bugby, 1999). The presence of orange/ red stains depicts the presence of fatliquors within the cross-sections of the leather samples B, C and D in contrast to A which was processed without fatliquor (Figure 6). Sample C also showed a high level of penetration of the prepared sulphonated oil within the leather. SCSO obviously compared favourably with the commercial fatliquor – Positive Control.

Scanning Electron Microscopy (SEM) Results

Figure 7 shows the surface morphology of the leather samples. From the SEM analysis results, the leather samples fatliquored with commercial fatliquor (positive control), prepared sulphonated fatliquor and its blend with 7.5% raw castor oil exhibited well opened

up structures. In contrast, the leather which was not fatliquored had a split up structure but the fibres restuck after drying. The well opened up fibre structure depicts good lubrication.

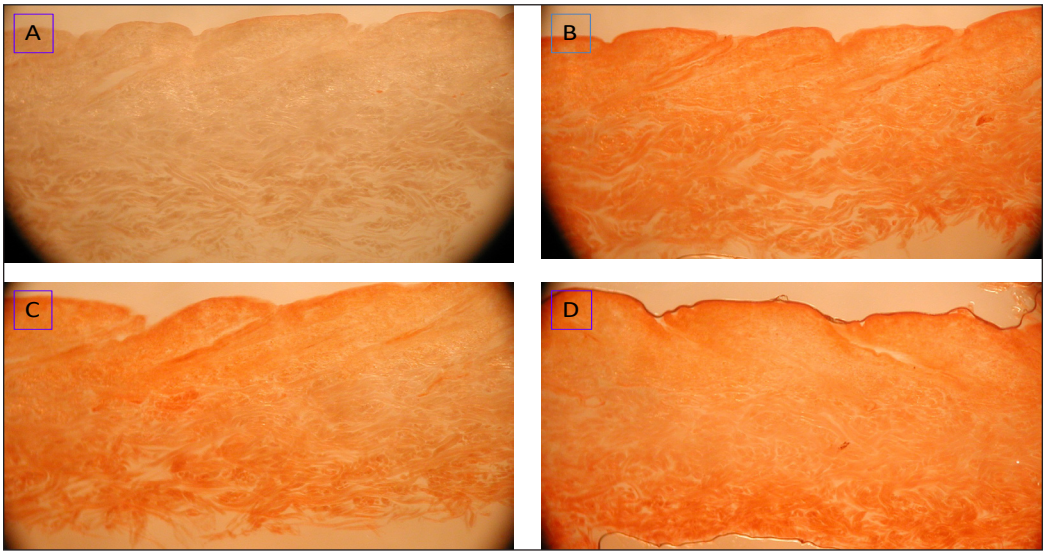


Figure 6. Staining Test Results Showing Cross-Section of Chrome Tanned Goatskins Processed with: **A**-NC; **B**- PC; **C**- A1 (PURE); **D**- A2 (BLEND)

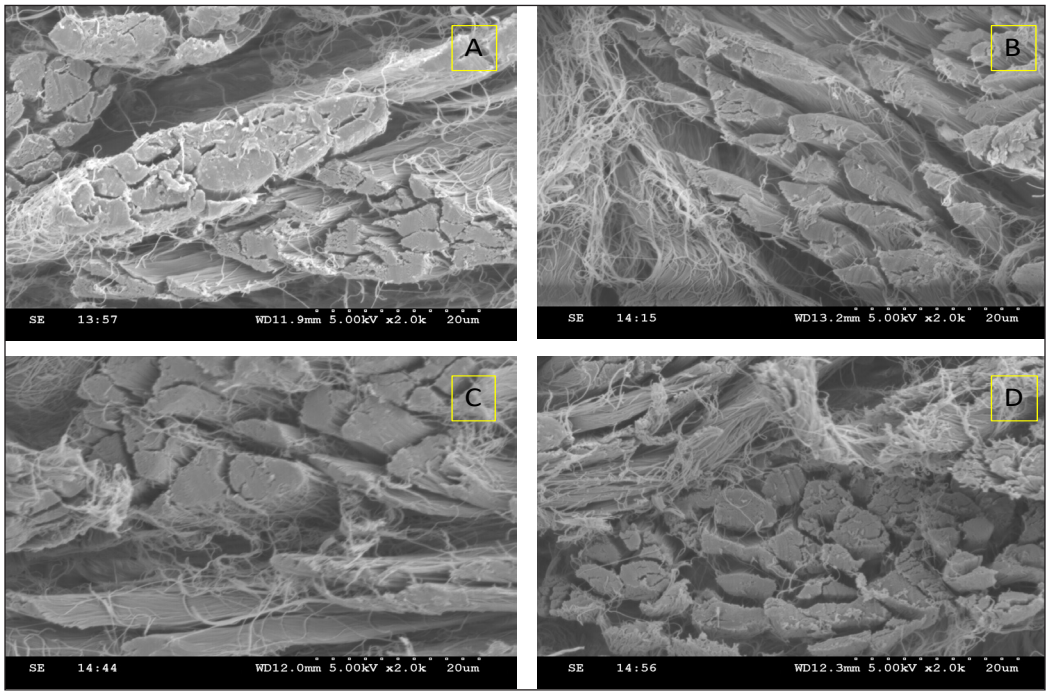


Figure 7. Scanning Electron Microscopy (X2000) of Chrome Tanned Goatskins Processed with: **A**-NC; **B**- PC; **C**- A1 (PURE); **D**- A2 (BLEND)

CONCLUSION

Structural characterizations performed by FT-IR, ^{1}H NMR and ^{13}C NMR analysis confirmed the sulphonation of CSO. It was observed from DSC results that both the CSO and SCSO were relatively thermally stable at the temperatures studied and would not likely decompose when being processed or in use as leather. The leather processed by the sulphonated *C. schweinfurthii* fatliquor had a comparable tensile strength, double edge tear, and grain strength with commercial/imported fatliquor. The stain test result showed the full lubrication of the *C. schweinfurthii* fatliquored leather and is comparable with leather from commercial fatliquor. This indicates that the sulphonated *C. schweinfurthii* fatliquor could be a rival with commercial products for the production of leather shoe upper.

ACKNOWLEDGEMENTS

The authors thank the management and staff of the Institute for Creative Leather Technologies (ICLT), University of Northampton, (UoN) Northampton, United Kingdom, for the support in terms of facilities, equipment and bench space offered for the work.

REFERENCES

Abayeh, O. J., Abdulrazaq, A. K., & Olaogun, R. (1999). Quality characteristics of *Canarium schweinfurthii*. *Plant Foods for Human Nutrition, 54*(1), 43-48.

Adewuyi, A., Awolade, P. O., & Oderinde, R. A. (2014). *Hura crepitans* seed oil: Alternative feedstock for biodiesel production. *Journal of Fuels, 2014*, 1-9.

Alexander, K. T. W., Corning, D. R., Covington, A. D., Stanley, A. M., & Stosic, R. G. (1993). The production of soft leather part 2: Drying and stress softening. *Journal of American Leather Chemists Association, 88*(7), 254-269.

Berg, M. J., Tymoczkko, J. L., & Styrer, L. (2002). *Biochemistry* (5th Ed.). New York, USA: W.H. Freeman Publishing.

BS 1723. (2015). *Leather, physical and mechanical tests: Determination of softness*. London, UK: British Standards Institution.

BS 2418. (2002). *Chemical, physical and mechanical and fastness tests: Sampling location*. London, UK: British Standards Institution.

BS 2419. (2002). *Chemical, physical and mechanical and fastness tests: Conditioning*. London, UK: British Standards Institution.

BS 3376. (2011). *Leather, physical and mechanical tests: Determination of tensile strength and percentage extension*. London, UK: British Standards Institution.

BS 3377. (2011). *Leather, physical and mechanical tests: Determination of tear load. Double edge tear*. London, UK: British Standards Institution.

BS 3379. (2015). *Leather, physical and mechanical tests: Determination of distension and strength of surface* (Ball Burst method). London, UK: British Standards Institution.

Bugby, A. (1999). Microscopy. In Leafe, M. K. (Ed.), *Leather technologists pocket book* (pp. 311-337). Withernsea, UK: Society of Leather Technologists and Chemists.

Burgess, D. (1993). General aspects of fatliquoring: An introduction to the application and chemistry of fat liquoring. *Journal of the Society of Leather Technologists and Chemists, 78*(2), 39-43.

Covington, A. D. (2011). *Tanning chemistry: The science of leather*. Cambridge, UK: Royal Society of Chemistry Publishing.

Daniels, R. P. (2001). Fatliquoring and softening agents. *World Leather, 14*, 68-70.

Evans, J. (2004). *Plantation forestry in the tropics* (2nd Ed.). London, UK: Oxford University Press.

Fashina, O. O., Craig-Schmidt, M., Colley, Z., & Hallman, H. (2008). Predicting melting characteristics of vegetable oils from fatty acid compositions. *Food Science Technology, 41*(8), 1501-1505.

Firestone, D. (1998). *Official methods and recommended practices of the American oil Chemists society* (15th Ed.). Champaign-Illinois, USA: American Oil Chemists Society.

Gunstone, F. D. (2004). *The chemistry of oils and fats: Sources, composition, properties and uses*. Oxford, UK: Blackwell Publishing Ltd.

Habib, M. A., & Alshammari, A. G. (2014). Leather fatliquor from hide fleshing. *Journal of the Society of Leather Technologists and Chemists, 98*(5), 199-203.

Heidemann, E. (1993). *Fundamentals of leather manufacturing*. Darmstadt, Germany: Eduard Roether KG Publishing.

ICLT SR15/31. (2015). *Leather manufacture: Shoe upper-chromium (non-compact).* Manual for Leather Processing. Northampton, UK: Institute for Creative Leather Technologies.

Janakiram, C. R. (2007). The theory and practice of fatliquoring. *World Leather, January edition*, 38-43.

Kaisersberger, E. (1989). DSC investigations of the thermal characterization of edible fats and oils. *Thermochim Acta*, *151,* 83-90.

Okieimen, F. E., Pavithran, C. & Bakare, I. O. (2005). Epoxidation and hydroxlation of rubber seed oil: One-pot multi-step reactions. *European Journal of Lipid Science and Technology, 107*(5), 330-336.

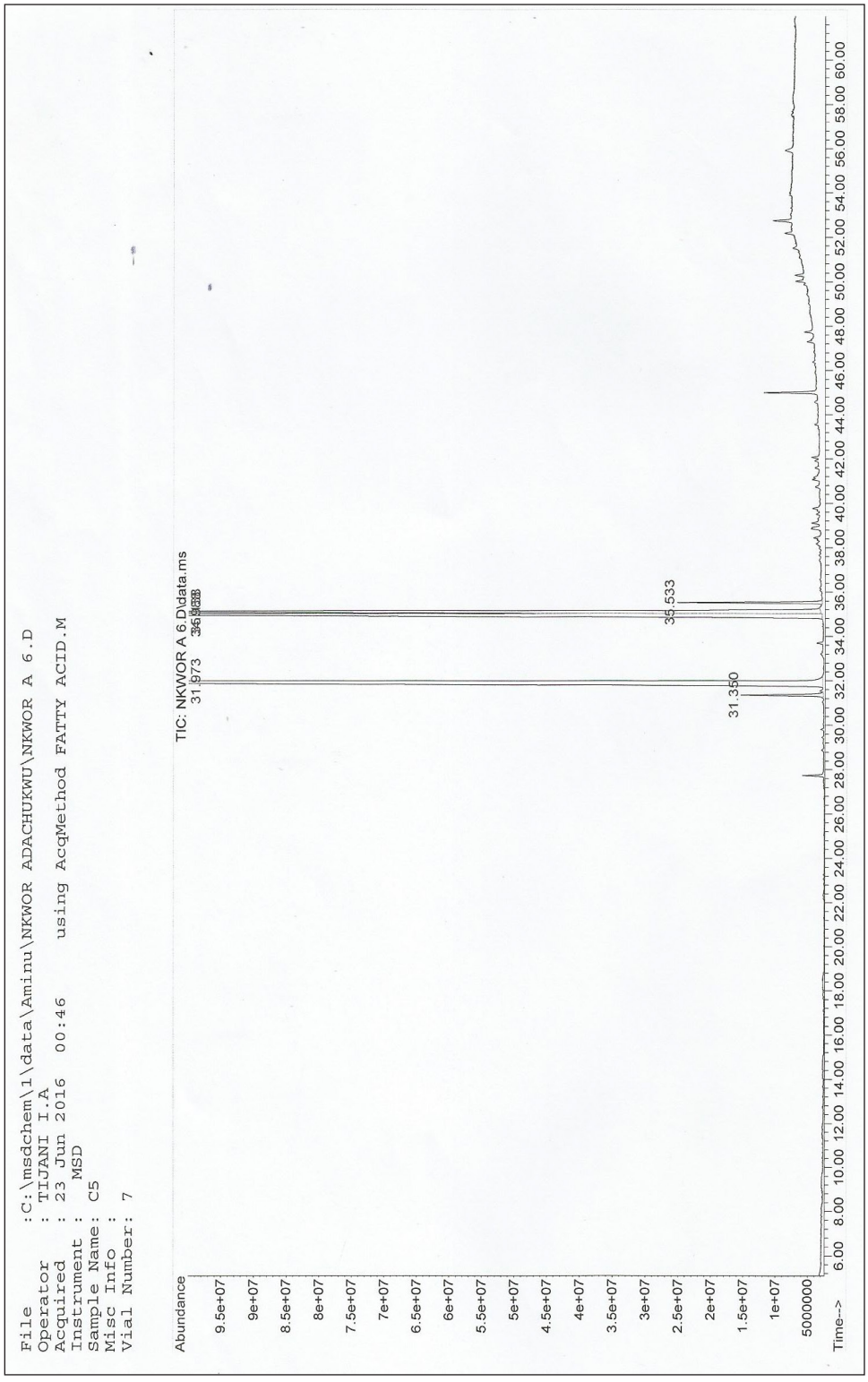
Sega, A., Zanardi, I., Chiasserini, L., Gabbrielli, A., Bocci, V., & Travagli, V. (2010). Properties of sesame oil by detailed ^{1}H and ^{13}C NMR assignments before and after ozonation and their correlation with iodine value, peroxide value and viscosity measurements. *Chemistry and Physics of Lipids, 163*(2), 148-156.

Steik, K. T. (1943). *U.S. Patent No. 2,328,931*. Washington, DC: U.S. Patent and Trademark Office.

Waite, T. (1999). Oils, fats, waxes and fatliquors. In Leafe, M. K., (Ed.), *Leather technologists pocket book* (pp. 125-148). Withernsea, UK: Society of Leather Technologists and Chemists.

APPENDIX A

Gas chromatogram of CSO methyl ester



APPENDIX B

Area percent report of CSO methyl ester

CHEMICAL ENG`G LAB.UNILORIN. Area Percent Report

Data Path : C:\msdchem\1\data\Aminu\NKWOR ADACHUKWU\
Data File : NKWOR A 6.D
Acq On : 23 Jun 2016 00:46
Operator : TIJANI I.A
Sample : C5
Misc :
ALS Vial : 7 Sample Multiplier: 1

Integration Parameters: rteint.p
Integrator: RTE
Smoothing : ON Filtering: 5
Sampling : 1 Min Area: 3 % of largest Peak
Start Thrs: 0.2 Max Peaks: 100
Stop Thrs : 0 Peak Location: TOP

If leading or trailing edge < 100 prefer < Baseline drop else tangent >
Peak separation: 5

Method : C:\Users\admin\Desktop\METHODS\ESSENTIAL OILS_SCAN2.M
Title :

Signal : TIC: NKWOR A 6.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	31.350	4699	4722	4746	rBV2	12743186	53852393	4.06%	1.699%
2	31.973	4783	4834	4866	rBV4	149858768	1325676903	100.00%	41.812%
3	34.988	5338	5376	5385	rBV6	124954707	953797339	71.95%	30.083%
4	35.138	5385	5403	5432	rVB2	142093213	752829976	56.79%	23.745%
5	35.533	5458	5474	5503	rVB2	22362273	84379940	6.37%	2.661%

Sum of corrected areas: 3170536551

SSENTIAL OILS_SCAN2.M Fri Jun 24 08:57:10 2016

APPENDIX C

Library search report of CSO methyl ester

CHEMICAL ENG`G LAB.UNILORIN. Library Search Report

Data Path : C:\msdchem\1\data\Aminu\NKWOR ADACHUKWU\
Data File : NKWOR A 6.D
Acq On : 23 Jun 2016 00:46
Operator : TIJANI I.A
Sample : C5
Misc :
ALS Vial : 7 Sample Multiplier: 1

Search Libraries: C:\DATABASE\demo.l Minimum Quality: 15
C:\Database\NIST11.L Minimum Quality: 90

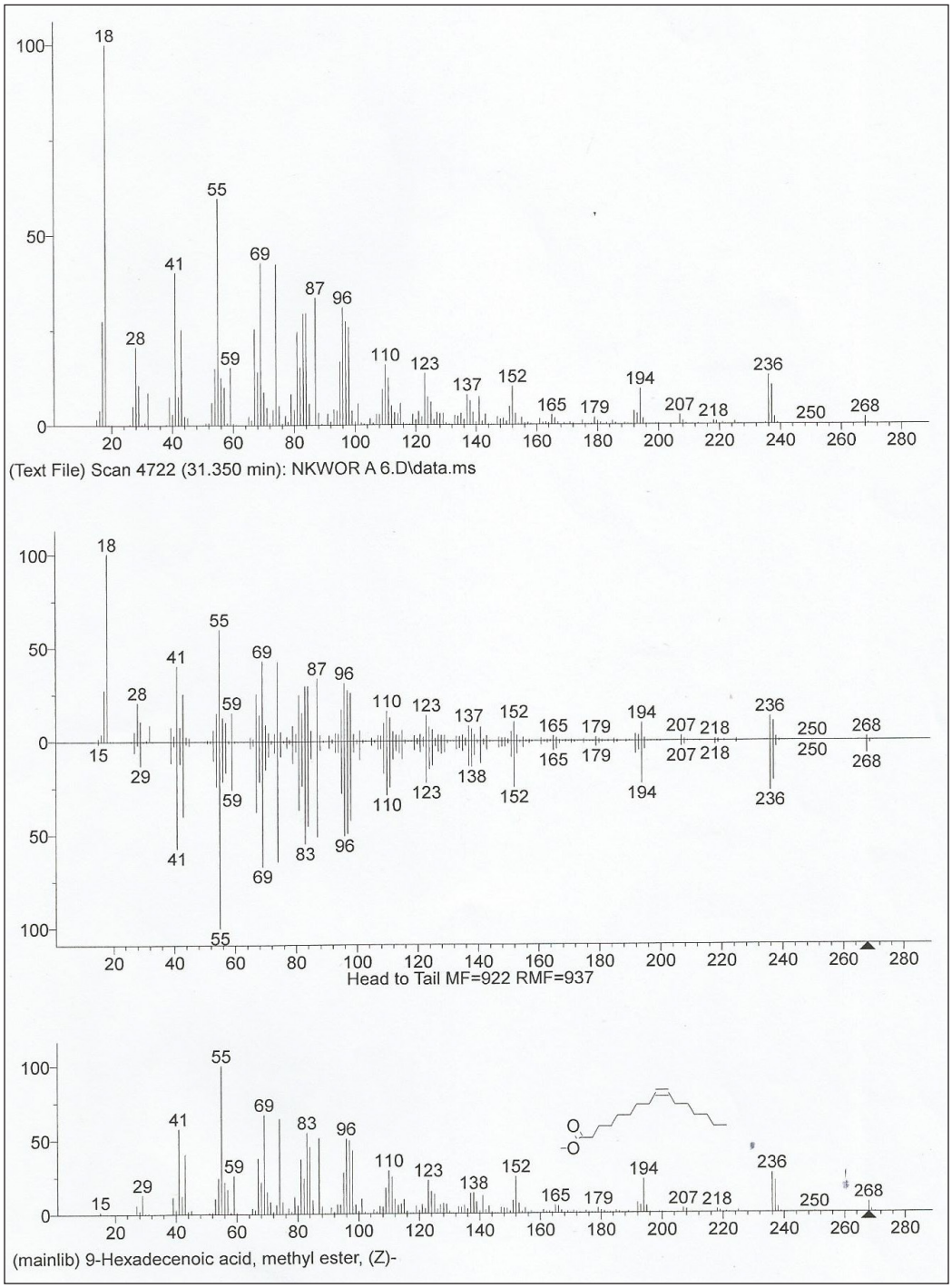
Unknown Spectrum: Apex minus start of peak
Integration Events: RTE Integrator - lscint.e

Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	31.350	1.70	C:\Database\NIST11.L			
			7-Hexadecenoic acid, methyl ester, (Z)-	117506	056875-67-3	99
			9-Hexadecenoic acid, methyl ester, (Z)-	117513	001120-25-8	98
			9-Hexadecenoic acid, methyl ester, (Z)-	117511	001120-25-8	98
2	31.973	41.81	C:\DATABASE\demo.l			
			Methyl palmitate	4	000112-39-0	70
3	34.988	30.08	C:\Database\NIST11.L			
			9,12-Octadecadienoic acid (Z,Z)-, methyl ester	139724	000112-63-0	99
			9,12-Octadecadienoic acid, methyl ester	139708	002462-85-3	99
			9,12-Octadecadienoic acid, methyl ester, (E,E)-	139733	002566-97-4	98
4	35.138	23.74	C:\Database\NIST11.L			
			14-Octadecenoic acid, methyl ester	141287	056554-48-4	99
			11-Octadecenoic acid, methyl ester, (Z)-	141313	001937-63-9	98
			9-Octadecenoic acid, methyl ester, (E)-	141309	001937-62-8	97
5	35.533	2.66	C:\DATABASE\demo.l			
			Methyl palmitate	4	000112-39-0	72

ESSENTIAL OILS_SCAN2.M Fri Jun 24 08:57:20 2016

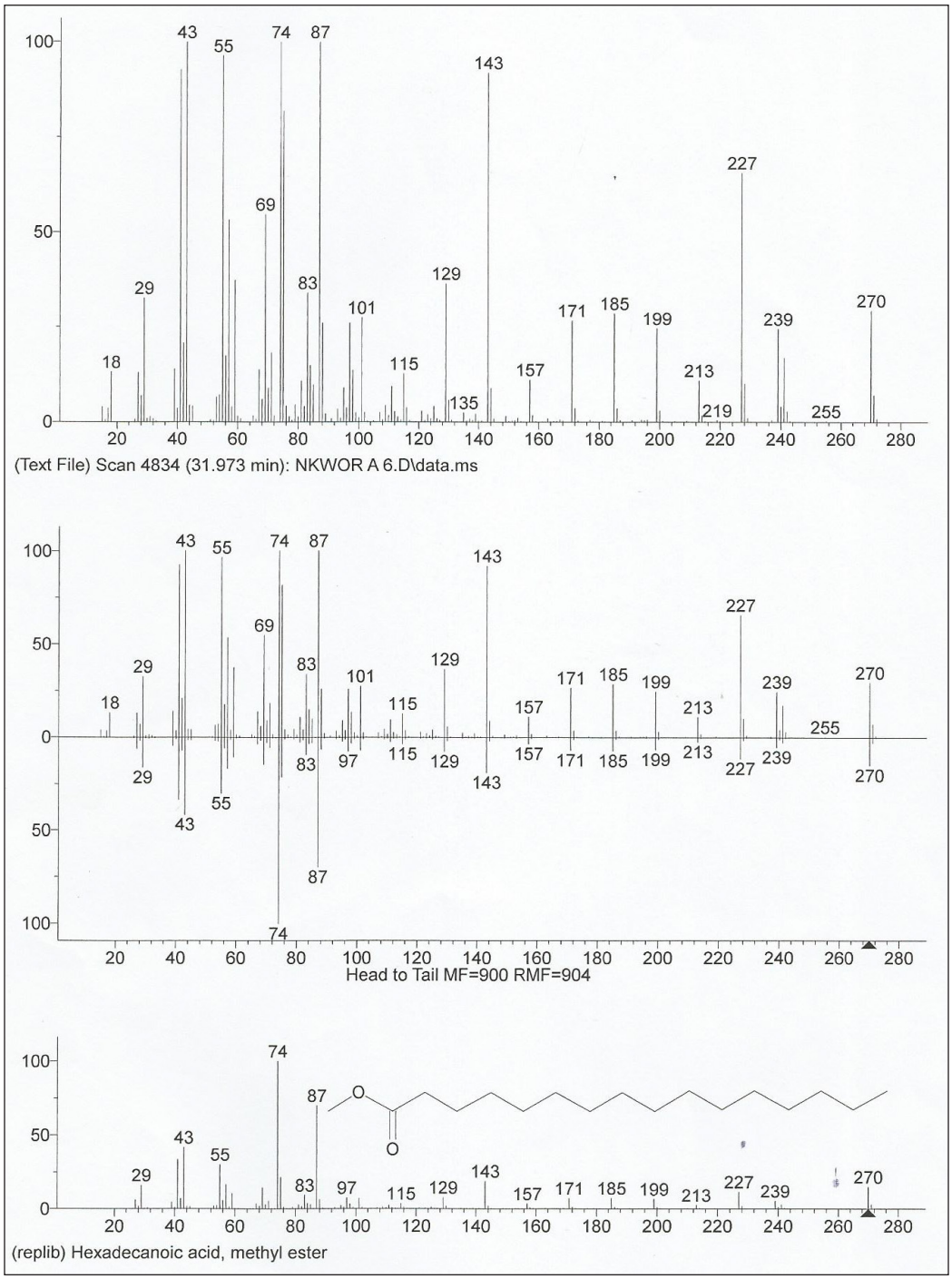
APPENDIX D

CSO methyl ester- mass spectrum for area percent (1.699 %, 31.350 min)



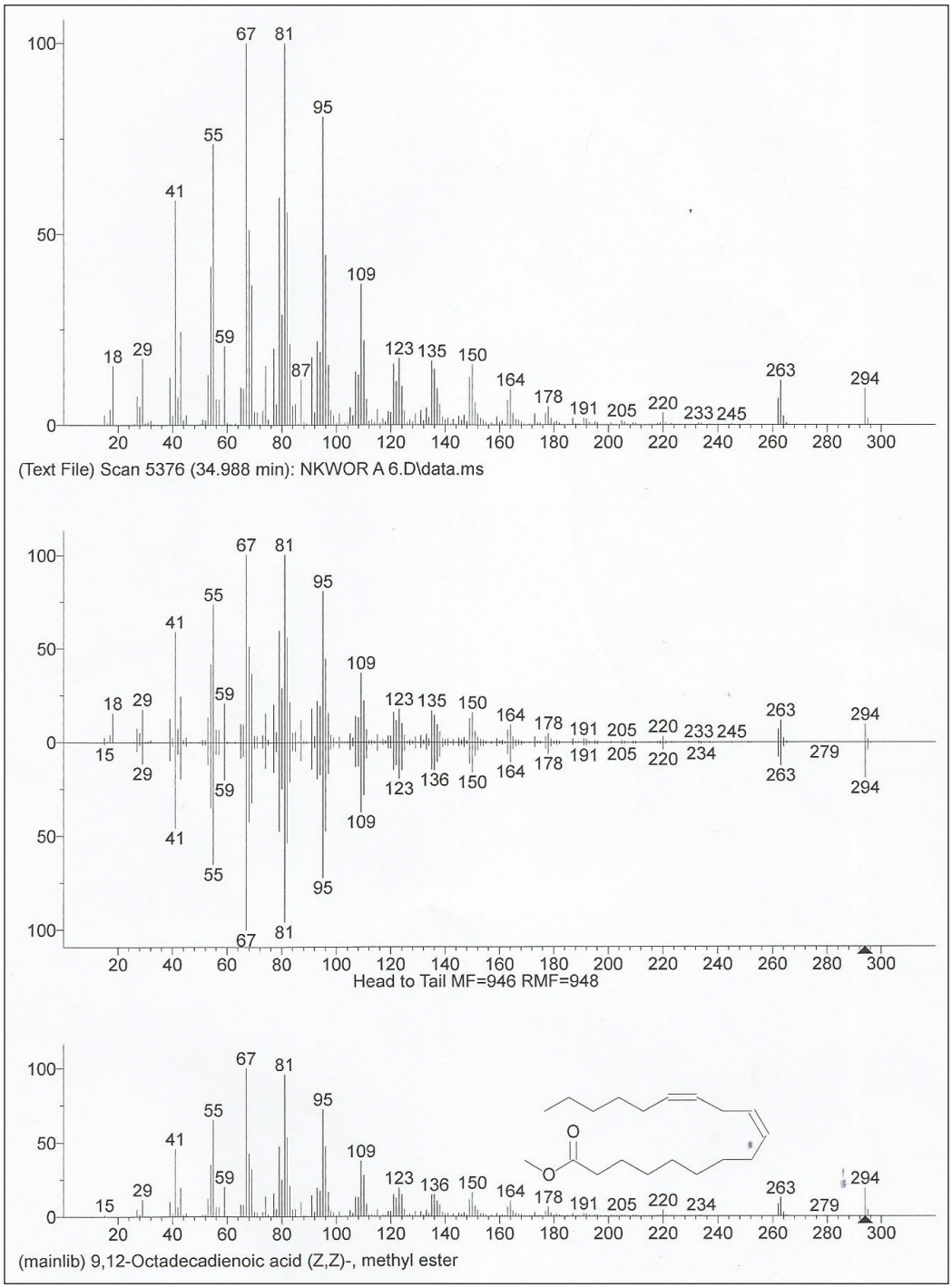
APPENDIX E

CSO methyl ester- mass spectrum for area percent (41.81 %, 31.973 min)



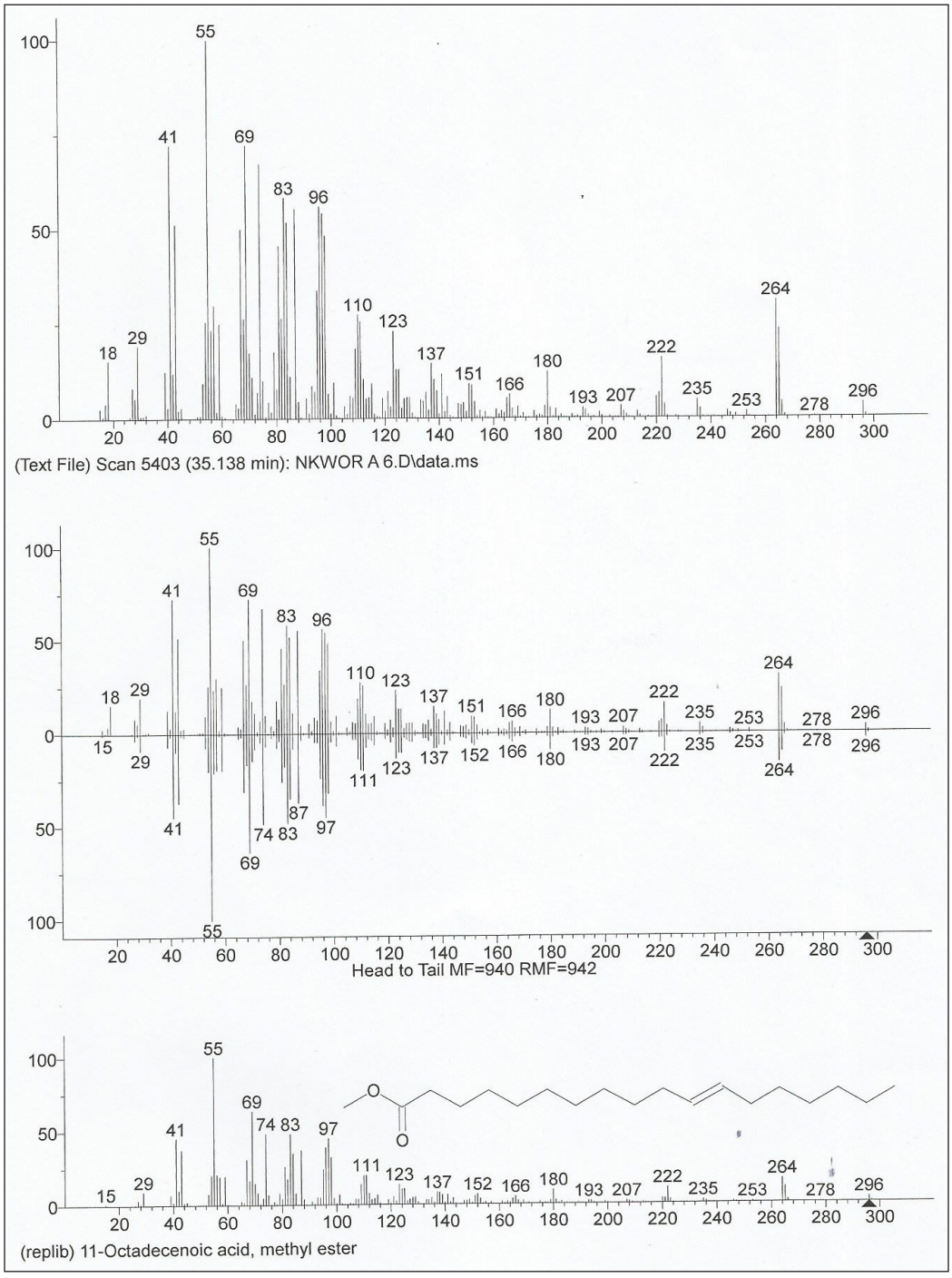
APPENDIX F

CSO methyl ester- mass spectrum for area percent (30.08 %, 34.988 min)



APPENDIX G

CSO methyl ester- mass spectrum for area percent (23.74 %, 35.138min)



APPENDIX H

CSO methyl ester- mass spectrum for area percent (2.66 %, 35.533 min)