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Characterisation of Turkey red oil by ^{1}H and ^{13}C NMR spectroscopy: Research on historical Turkey red dyeing for re-creation, conservation, and understanding

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Abstract

Heritage conservation science is a valuable technique for the improved understanding and preservation of historical objects. Material analysis of heritage textiles and related materials provides information about polymer and colourant degradation, and contribute to improved conservation and display practices. The re-creation of materials following historical processes is useful to test analytical techniques in a field where ethical constraints often make sampling limited, and to identify potential age-related changes relative to a 'fresh' product. Despite the broad historical interest and industrial significance of Turkey red from the late 18th through the 19th c., little about the chemical complex of these unique textiles was understood in scientific terms. This research applied modern analysis by ^{1}H and ^{13}C NMR spectroscopy to investigate the conclusions by 19th c. chemists that fatty acids were the important component of the oil treatment, a unique and vital aspect of the Turkey red dyeing process. The results show the Turkey red oil samples are composed of fatty acids, which tend to polymerise over time, and that modern commercial Turkey red oil has a similar composition to historical samples and a replica sample made following a 19th c. method. This information was used to form a hypothesis for the overall Turkey red complex on the fibre, and confirmed the experimental work of 19th c. chemists was theoretically accurate despite their lack of precise analytical techniques. This indicates a recreation and analysis approach is effective for studying heritage materials provided the historical practice for making the original object is considered.

Introduction

The vivid hue of Turkey red textiles has long been attributed to the unusual pre-treatment of the fibres with an oil bath,[1,2] which was acknowledged as imperative to a successful dyeing.[3,4] The method, also called Turkey red, was a long and complicated process that required expert knowledge [5] and produced red cloth of legendary fastness to light exposure, washing, rubbing, and bleaching.[6,7] Research and experiments on Turkey red by eminent early chemists like Chaptal [8] and Berthollet [9], and continued investigations throughout the 19th c. [10,11] contributed to a partial understanding of Turkey red, but many questions persisted into the beginning of the 20th c. when improved azo dyes brought about the decline of the Turkey red industry.[5]

Turkey red was dyed on 'vegetable' or cellulosic fibres, though primarily on cotton as linen required more work to dye.[3] The process uses oil, aluminium, calcium, and madder or alizarin dye (hydroxyanthraquinone) to form the Turkey red complex. The oil pre-treatment is a unique characteristic of Turkey red dyeing not seen in other colours or practices, though it is occasionally used elsewhere as a finishing agent. From the establishment of the first European Turkey red works in Europe in 1747 [12], Turkey red oiling was done with an emulsion of rancid olive oil (*huile*

tournante) and weak aqueous sodium carbonate, with and without ruminant dung additive. This became known as the 'old' process in the late 19th c., in contrast with the 'new' process that used Turkey red oil (TRO) [4], which came into use around 1870-1875.[13,14] It was the first synthetic anionic surfactant [15] and made it possible to shorten the oiling phase from three treatments to one [2] and the overall process from weeks to days.[16] Turkey red oil was manufactured by reacting castor oil with sulfuric acid for a specific period, then washing out the excess acid and neutralising the oil with a strong base like sodium hydroxide.[17] Although Turkey red is no longer commercially produced, Turkey red oil is still employed as a finishing agent to give softness and drape to cellulose fabrics,[18] as a lubricant, to make inks and industrial detergents, and to treat leather.[19] As such, Turkey red oil is still commercially available today. The literature on Turkey red oil analysis [20,21] addresses its surfactant properties in a modern context, and does not make any connections to historical processes or the Turkey red dyeing process for which this oil was originally developed.

By the second half of the 19th c., dyers and chemists were confident from their experiments that the effectiveness of the oil bath depended on its fatty acid content.[10,17,22] In naturally rancid olive oil, the fatty acid content depends on the natural breakdown of triglyceride oils. Oiling in the 'old' process involved a much lower proportion of fatty acids relative to oils and partial glycerides, making more repetitions necessary and increasing the need to wash the excess oil from the fabric. In contrast, Turkey red oil was thought to have had a higher fatty acid content from the more complete glyceride hydrolysis by sulfuric acid and was water soluble, making application and washing more efficient. The transition from the 'old' to 'new' Turkey red process was a significant technological advance for the industry, but did not change the fundamental chemistry of the process.[23] Turkey red oil could be made on-site, which was useful to save freight costs and because the fatty acids would polymerise with time,[13] forming compounds called estolides that decreased its usefulness in dyeing.

Today, the legacy of the Turkey red industry in Scotland, which once employed thousands,[5] is the collections of textiles held in museums and archives. Heritage textiles can be difficult to display since exposure to light tends to degrade colours and fibres. The purpose of this research is to improve our understanding of the Turkey red complex on these unique textiles through modern conservation-based analysis, and to eventually determine how to optimally display and conserve Turkey red to increase collection accessibility and longevity. In this paper, the composition of Turkey red oil samples from a variety of modern and historical sources are analysed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. These results support previous conclusions about its composition from on 19th c. experiments with instrumental analytical data, laying the foundation for an understanding of the overall Turkey red complex.

Experimental

1.1.1.1 Reagents and references

Castor oil (reagent grade), sodium sulfate (Na_2SO_4, anhydrous reagent grade), and toluene (analytical grade) were purchased from Fisher (UK); conc. sulfuric acid (H_2SO_4, ACS grade 95.0%-98.0%) and ricinoleic acid (≥99%) were purchased from Sigma-Aldrich (UK); sodium hydroxide (NaOH, analytical grade) was purchased from Acros Organics (UK); ultrapure water (18.2 MΩ resistivity) was obtained from a Millipore Direct-Q UV 3 water purifier; Turkey red oil sodium salt (microscopy grade), phenolphthalein (indicator grade) and ethanol (IMS) were purchased from Fluka (UK); chloroform-d ($CDCl_3$) was purchased from Cambridge Isotope Laboratories (UK); a sample of coco-oleic estolide-2-ethylhexyl esters (estolides) was donated by Dr Steven Cermak at the USDA Agricultural Research Service (Peoria, IL, USA).

1.1.1.2 Replica Turkey red oil

A sample of Turkey red oil (Figure 1) was prepared following a method published in *A Manual of Dyeing* (1893) [17] and related texts from the literature.[13,14,20] In a glass beaker, 54.4 g castor oil was weighed and 18.1 g H_2SO_4 added in 1 mL increments while stirring, resting 20 minutes between additions to dissipate heat. The mixture, which became opaque, dark brown and less viscous,

was left overnight to react. A solution of 400 mL ultrapure water was heated to 40 °C and the oil added and stirred. The colour became creamy, pale yellow and separated into two phases. It was decanted into a separating funnel and the lower aqueous layer drained away. The oil was washed again with 400 mL of 0.9 M aq. Na_2SO_4 and left overnight, then the biphasic layers stirred again and left to separate as before. A solution of 3.5 M aq. NaOH was prepared to neutralise the remaining acid and about 1.5 mL was added to the oil, a few drops at a time, stirring between additions until completely mixed. The addition was complete after clear pockets began to appear in the opaque oil, eventually persisting until the oil was transparent and deep yellow. Diluting a drop of oil in 1 mL of ultrapure water tested within the acceptable range of pH 7-8, and the oil (TRO Replica) was considered finished.

1.1.1.3 Historical Turkey red oil samples

Two samples of historical Turkey red oil were donated for this research. The first, of uncertain provenance (proposed early 20th c.), was donated by dyer Debbie Bamford (TRO DB) and is said to have come from a Turkey red dyer. The sample is semi-opaque, deep yellow, and like a gel in consistency. The second comes, from the collection of the Society of Dyers and Colourists at Perkin House in Bradford, UK, (TRO SDC) and dates from the late 19th c. (Figure 2). The sample is dark brown and highly viscous.

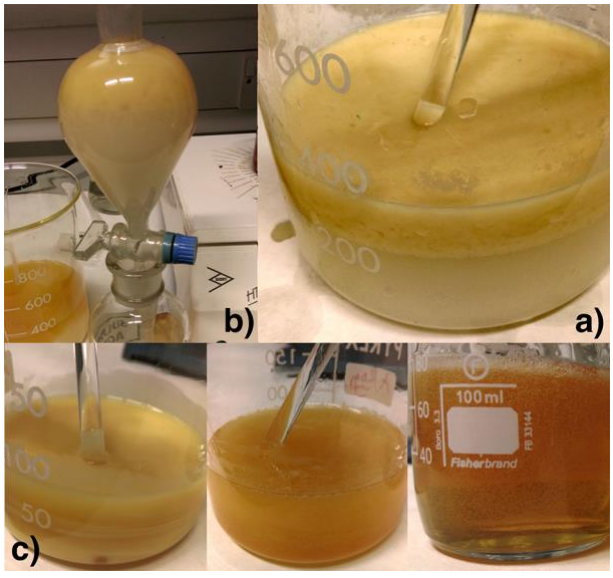

Figure 2 The replica Turkey red oil a) after washing with water, b) being separated from the aq. phase and c) during neutralisation with aq. NaOH (from left: initial, partially neutralised, final).

Figure 1 Bottle of 19th c. Turkey red oil in the Society of Dyers and Colourists collection, Perkin House (Bradford, UK). Image courtesy of the Society of Dyers and Colourists.

1.1.1.4 NMR sample preparation

For the castor oil, ricinoleic acid, and estolides references, one drop of sample was added to 1 mL of $CDCl_3$ along with a few milligrams of Na_2SO_4 to dry any residual water. After shaking, the sample was filtered through cotton wool into an NMR tube. The commercial Turkey red oil from Fluka (TRO Fluka), TRO Replica, TRO DB, and TRO SDC contained more water from the manufacturing process and required

drying with a toluene azeotrope. About 20 mL toluene and 2-3 drops of sample were swirled together in a 100 mL round-bottom flask until the oil was dissolved, then the solvent evaporated on a Buchi Rotovapor under vacuum until the volume was constant. This was repeated once and after the second evaporation the sample was reconstituted from the walls of the flask by swirling 1 mL $CDCl_3$ and then filtering the solution through cotton wool to trap particulates. A second castor oil sample was dried this way to confirm consistency and a blank sample was prepared to show no residual toluene peaks interfered with interpretation.

Spectra were acquired on a Bruker AVII 500 MHz NMR spectrometer at 500 MHz for ^{1}H spectra and at 125 MHz for ^{13}C spectra. The accompanying TopSpin software from Bruker was used to process the spectra.

1.1.1.5 Acid value

Acid values were determined by titration for castor oil, TRO Replica, TRO Fluka, and TRO DB [24]. An indicator solution of 1% phenolphthalein in 1:1 v/v ultrapure water and ethanol was prepared. A portion of this was added to a larger volume of the same solvent and titrated with 0.10 M aqueous NaOH until very slightly pink. A 50 mL portion of this neutralised solvent plus 1 mL indicator were used to dissolve samples weighing about 5.0 g (10.0 g for castor oil; prepared in neutralised 100% ethanol). These were titrated with 0.1 M aqueous NaOH with constant stirring until the endpoint, and each oil was titrated in triplicate.

Results and discussion

Castor oil, the starting material to make Turkey red oil, is composed of triglycerides containing ca. 87% ricinoleic acid, or 12-hydroxy-9-*cis*-octadecenoic acid, with the remainder other long-chain fatty acids.[21] Figure 3 shows the structure of triricinolein, with the glycerol backbone and ricinoleic acid carbons numbered, and Figure 4 shows a numbered triricinoleic estolide. The mixed fatty acid composition in castor oil and the reaction with sulfuric acid produces a mixture for which it is difficult to assign precise chemical shift values and coupling constants, and this is not attempted in this work. Peak ranges are referred to when signals are from similar compounds in the sample mixture, and

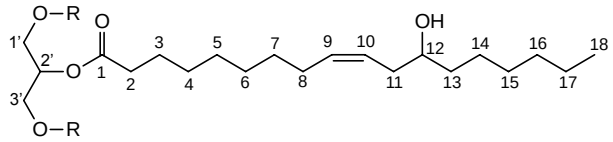

Figure 3 Carbon positions numbered on triglyceride molecule with ricinoleic acid.

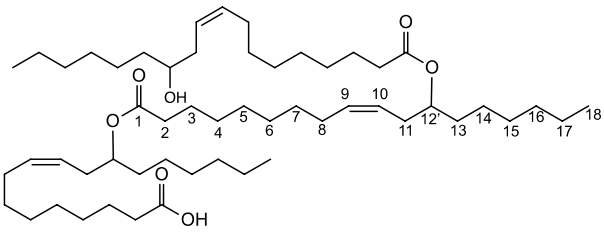

Figure 4 Carbon positions numbered on triricinoleic acid estolide.

the full, integrated spectra from which the figures are taken are included in the supplemental information. The analysis was used to confirm by modern standards that Turkey red oil is comprised of free fatty acids, based on 19th c. research and literature, so that further analysis of the Turkey red complex on cotton fibres can be undertaken with confidence.

The ^{1}H NMR spectra for references castor oil and ricinoleic acid are consistent with published spectra [25–27]. In Figure 5, the spectra for castor oil, ricinoleic acid, and the TRO samples show the effect of the reaction with H_2SO_4. From the left, the peaks for H9/H10 and H2' of alkenes and glycerol protons (5.22-5.55 ppm), H12' of estolides (4.75-4.85 ppm), H1' and H3' of glycerol protons (4.11-4.29 ppm), and H12 carbinol (3.56-3.65 ppm) (see Figure 3) are presented.

The contrast between the H9/H10 and H2' signals in castor oil and ricinoleic acid versus the TRO samples is consistent with changes to the proton environments, resulting in amorphous signals that have indistinct spin coupling. Castor oil is the only sample with a clear H2' signal; in the mixed TRO samples, it becomes a shoulder on the alkene peaks. The formation of the H12' peak (Figure 4) around 4.87 ppm indicates the formation of estolides, which Hawke and Kohll found formed best at high temperatures but would also form over a longer period at room temperature.[28] Estolide formation between FFAs in Turkey red oil decreases the efficacy of the oil treatment by reducing the amount

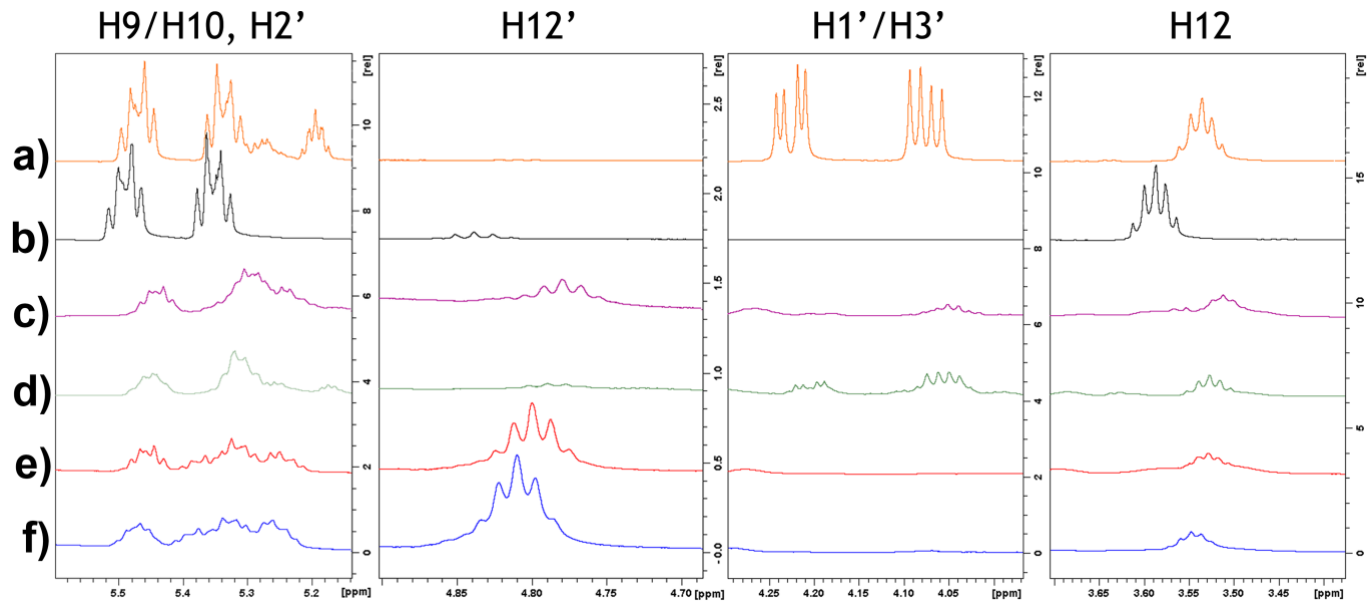

Figure 5 Sections of 1H NMR spectra for a) castor oil, b) ricinoleic acid, c) TRO Fluka, d) TRO Replica, e) TRO SDC, and f) TRO DB in CDCl3. Note different vertical scales for peak visibility.

of FFAs available to bond to the cellulose, and is an indicator of sample age and storage conditions relative to freshly made Turkey red oil. The older TRO SDC and TRO DB samples have signals here clearly visible above the baseline, having had more time to form estolides, while in the other TROs (except castor oil) the peaks are less distinct.

The signals from the H1' and H3' glycerol protons are easily identified in castor oil and absent, as expected, in ricinoleic acid. The spectra for TRO Fluka and TRO Replica appear to have traces of glycerol present between 4.22-4.29 ppm, and in TRO SDC and TRO DB no obvious peaks are visible. The H12 carbinol signal appears in castor oil at 3.58 ppm and in ricinoleic acid at 3.63 ppm due to the effect of the glycerol moiety in the triglyceride. All four TRO spectra have a carbinol peak as well; like the H9/H10 signals it is more amorphous than the corresponding castor oil spectrum due to the mixed sample composition. Turkey red oil is also called sulfated castor oil, implying that the product should contain a quantity of sulfated compounds. This would typically occur on the ricinoleic hydroxyl at C12 after the glycerol hydrolysis reaction, followed by any reactions with the alkene bond.[29] These compounds tend to hydrolyse during the neutralisation process [30,31], according to the literature. The spectra in this paper did not contain any peaks consistent with the results of a study comparing natural lipids with hydroxyl and sulfate ester groups [32] that conclusively indicated a significant portion of Turkey red oil was sulfated fatty acids.

The integrated areas in Table 1 show the peak areas from the proton environments in Figure 5, with the H12 carbinol set at 1.00 for all except the estolides, which do not contain ricinoleic acid. This spectrum is integrated to the H12' proton, to indicate degree of estolide formation in the samples relative to pure estolides. The data in the table indicates that in the TRO samples, relative to the remaining H12 protons in a sample, there is more unsaturation in TRO Fluka, Replica, and DB than in unreacted castor oil. The TRO SDC sample has slightly less, and this sample and DB have very little remaining glycerol as well. TRO Fluka has less than unreacted castor oil, while the Replica sample has a similar relative amount of H1'/H3' to H12. Compared to the pure estolides, the historical TRO SDC and DB samples have a higher degree of formation. TRO Fluka has more than Replica, and was manufactured a few years prior to this work. The increased unsaturation may be the result of sulfate esters forming and then hydrolysing, and the glycerol content indicates variable hydrolysis on this bond. The exact fatty acid and triglyceride composition in these samples is beyond the scope of this work, which focuses on the general composition of Turkey red oil for Turkey red dyeing.

	H9/H10 + H2'	H12'	H1'/H3'	H12
	5.22-5.55 ppm	4.87 ppm	4.11-4.29 ppm	3.59 ppm
Castor oil	2.8	0.00	1.52	1.00
Ricinoleic acid	2.11	0.01	0.00	1.00
Estolides	0.00	1.00	0.00	0.00
TRO Fluka	4.66	0.29	0.65	1.00
TRO Replica	3.00	0.09	1.47	1.00
TRO SDC	1.80	0.20	0.00	1.00
TRO DB	4.48	0.62	0.09	1.00

Table 1 Integrated areas under the curve of ^{1}H NMR spectra from Figure 5 (see supplemental information). Column headers denote proton environment and chemical shift of signal on the spectrum relative to TMS (0 ppm

The ^{13}C NMR spectra in Figure 6 show the same samples as in Figure 5. Peak assignments were consistent with published spectra for castor oil and ricinoleic acid.[25,27,33] In the two leftmost panels, peaks for C1 from free fatty acids and triglyceride fatty acids bound to C1' and C3' appear from 170-181 ppm and 173-174 ppm, respectively. The TRO Fluka and Replica samples have trace glycerol carbon signals as well, consistent with the ^{1}H spectra in Figure 5. The C1 of estolides appears at 174.0 ppm,[34] as shown in the TRO DB and SDC samples, and to a lesser extent in TRO Fluka. The central panel shows C12 around 71.5 ppm, shifted slightly upfield in castor oil due to its triglyceride composition. The next panel shows C1'/C3' from glycerides around 68.8 ppm, and the one on the right the peak for C2' around 62 ppm.

In Figure 7, the ^{13}C NMR spectra of the TRO samples are compared to the estolide reference, coco-oleic 2-ethylhexyl ester. The estolide C12' (see Figure 3) appears around 74 ppm, consistent with previous analyses [34]. Only TRO Replica, the freshest sample, did not have a clear C12' signal; in the ^{1}H spectrum in Figure 5 this signal was fairly weak.

Figure 8 shows the spectra for castor oil and ricinoleic acid compared to the TROs from 179-182 ppm, where the fatty acid C1 appears. In addition to the peak for C1 around 180 ppm in the TRO samples, TRO Fluka has an additional C1 signal at 182.6 ppm consistent with a fatty acid sodium salt. The spectra for TRO SDC and DB samples do not provide much useful information due to their low concentration.

The acid value for each sample was calculated from an average of the three replicates, using the equivalent amount of KOH based on the experimental results. The values are presented in Table 2. The theoretical acid values for pure oleic acid and pure ricinoleic acid, based on molar mass, are 198.03 and 187.39, respectively. The experimental results for the Turkey red oils fall between castor oil and pure fatty acids, indicating hydrolysis occurs but is not complete.

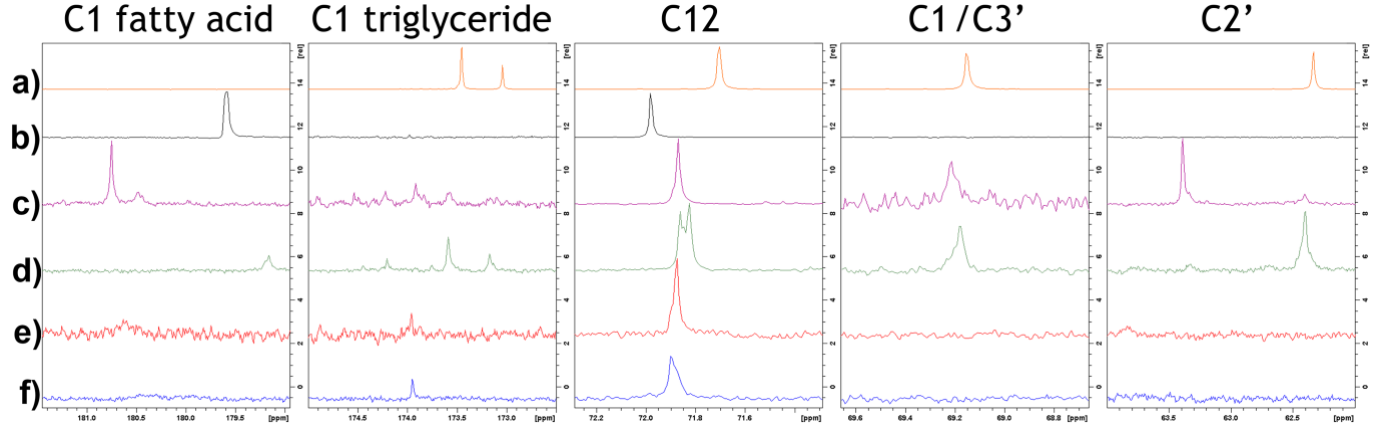

Figure 6 Sections of 13C NMR spectra for a) castor oil, b) ricinoleic acid, c) TRO Fluka, d) TRO Replica, e) TRO SDC, and f) TRO DB in CDCl3. Note different vertical scales for peak visibility. Spectra taken in CDCl3.

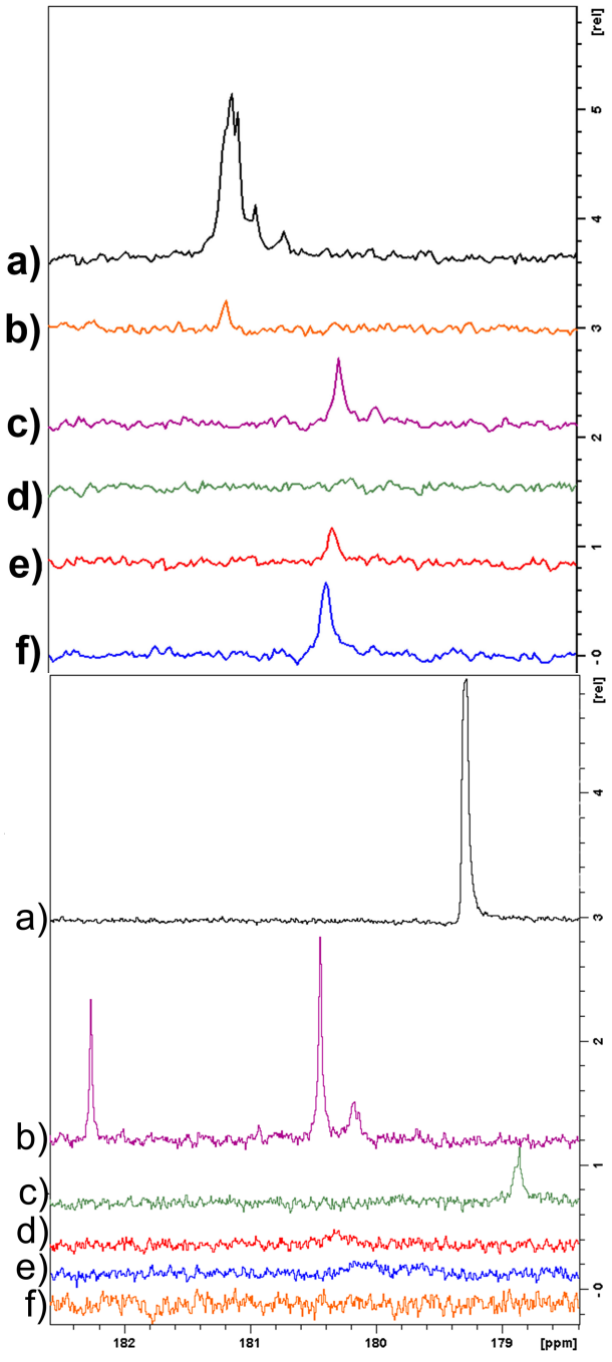

Figure 8 Sections of 13C NMR spectra for a) ricinoleic acid, b) TRO Fluka, c) TRO Replica, d) TRO SDC, e) TRO DB, f) castor oil. Spectra taken in CDCl3.

	Acid value
Castor oil	0.20
TRO Fluka	49.06
TRO Replica	51.12
TRO DB	23.24

Table 2 Acid values (mg KOH required to neutralise 1 g sample) determined by titration for oil samples.

Conclusion

The analysis of Turkey red oil samples by ^{1}H and ^{13}C NMR spectroscopy, using castor oil and ricinoleic acid as references, shows that castor oil triglycerides react with sulfuric acid during the manufacturing process to yield samples primarily composed of free fatty acids. Some samples have residual glycerol signals, indicating some, but not all, is removed in the washing. The sulfuric acid also reacts with fatty acid alkenes and hydroxyl groups, based on the analysis of the ^{1}H peaks for these environments when compared to castor oil and ricinoleic acid references. The fatty acids will autopolymerise over time, as indicated by the appearance of signals for estolide chain formation, H12' in the ^{1}H spectra and C12' in the ^{13}C spectra. The historical TRO SDC and TRO DB samples have a higher concentration of what are probably polyricinoleic estolides compared to the fresher TRO Fluka and Replica samples.

The chemists and dyers of the 19th c. who were interested in the composition and role of the oil made significant steps toward answering their questions through practical experimentation. They concluded that a high fatty acid content was desirable in the oil. In theory, pure fatty acids would be the most efficient oiling treatment, but their low water solubility makes them difficult to evenly distribute. Efforts to increase the efficiency of Turkey red dyeing yielded Turkey red oil, the first synthetic anionic surfactant, whose water solubility and increased fatty acid content was a great advantage to the industry. The re-creation and analytical investigation of Turkey red oil provides a basis for understanding the overall chemistry of the Turkey red complex and historical dyed textiles. A technique for analysing and identifying Turkey red textiles can be built from the information about Turkey red oil and fatty acids, which is useful to determine an analytical technique that can detect these compounds.[23] Understanding the chemistry of Turkey red and identifying Turkey red textiles is another step toward investigating and quantifying the light fastness of these textiles for more comprehensive collection care and display practices.

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