

Introduction

Increasingly, analytical chemistry is being used in the field of archaeology to characterize unknown compounds and confirm currently held hypotheses of the function of various artifacts. The current study focuses on a substance discovered inside an ancient Chinese artifact owned by the Ezkenazi Gallery in London. The artifact (Fig. 1a), is an ornate vessel made of gilt bronze dating from the Western Han dynasty (206 BC – 8 AD), and it has been tentatively identified as a lamp, perhaps for ceremonial use. The substance is a fairly homogeneous, waxy, cream-colored low-melting (61.5-63.5 C) solid with traces of green residue on the edges (probably from contact with oxidized surface of artifact). Simple solubility testing showed that the sample was highly hydrophobic and organic in nature, suggesting that it may be residue from fuel used in the lamp, perhaps even melted wax from a candle or cake. The solubility and melting point are consistent with beeswax (mp: 60-67 C).³

The chemical identification of the substance is of particular historical interest, since little is known about the types of fuels used for lighting such lamps. For example, beeswax candles are not generally thought to have been used for lighting in China until much later (> 600 AD). However, one Eastern Han dynasty text, the “Qian Fu Lun” (90-165 AD), has a suggestive reference to, “understanding the ability of oily insect wax to light lamps” (Fig. 1b). The goal of this project was to characterize the wax-like substance using analytical techniques, such as Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR). One complication is that a clear chain of custody cannot be established, so contamination from modern sources (e.g. a paraffin wax candle) must be ruled out before conclusions can be drawn about function of the artifact in ancient China.

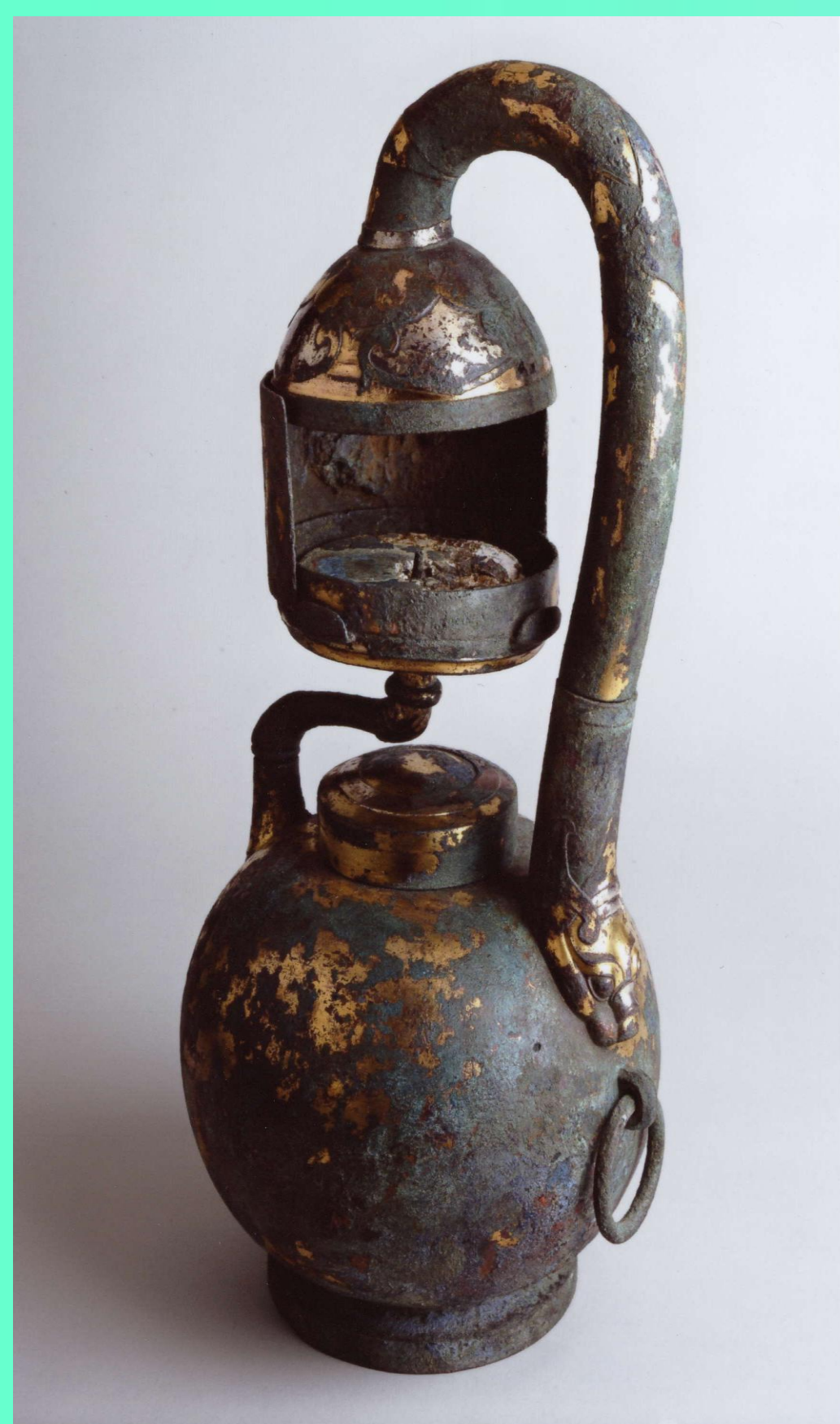


Fig.1a (left) Western Han Dynasty artifact from Ezkenazi Gallery (London).

Fig.1b (right) Excerpt from Qian Fu Lun text, referring to use of an “oily wax from an insect” to “light a lamp”

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Experimental Method

Infrared spectra were recorded using a Thermo-Nicolet 6700 FTIR spectrometer, equipped with a liquid nitrogen-cooled MCT-A detector. Samples were prepared by dispersing 9.8 mg of sample in Nujol or Fluorolube to make a mull, which was then spread between two KBr windows. The sample volume was purged with dry nitrogen to remove atmospheric water and CO₂. For the NMR spectra, ~5mg of sample was dissolved in 1 mL of deuterated chloroform, and placed in an NMR tube. Then ¹³C-NMR, ¹H NMR, and COSY-NMR were performed on the sample. For both techniques, care was taken to select material that was not contaminated by the green residue described above.

Results - FTIR

Figures 2a and 2b show FTIR spectra of the sample prepared with Nujol and Fluorolube, respectively. Reference spectra of the pure solvents are shown in blue for comparison. In both spectra there is a peak at ~1734.5 cm⁻¹, which is consistent with the carbonyl group of a wax ester.¹ Other bands in the 1100-1250 and 2800-3000 cm⁻¹ regions, are consistent with this assignment. There also appears to be a weak band in the OH-stretching region near 3400 cm⁻¹, which is consistent with a hydroxyl-ester. This is consistent with a natural product wax (e.g. beeswax) and rules out a pure hydrocarbon wax, such as paraffin or ceresin. Figure 3 shows FTIR spectra of four common waxes including paraffin wax, beeswax, carnauba wax, and lanolin wax.³⁻⁶ Each of the latter 3 waxes is a mixture of chemical compounds, the chief component of which is a monoester. Carnauba wax is derived from plants and is often used in cosmetics as an emulsifier. Fig. 3c does show an ester peak near 1734 cm⁻¹, it also exhibits a sharp peak near 1600 cm⁻¹, which is clearly absent from our spectrum. The spectrum of lanolin wax from sheep’s wool (Fig. 3d) and that of beeswax (Fig. 3a) are similar to one another and to our sample, requiring further analysis to refine the identification.

FTIR Spectra

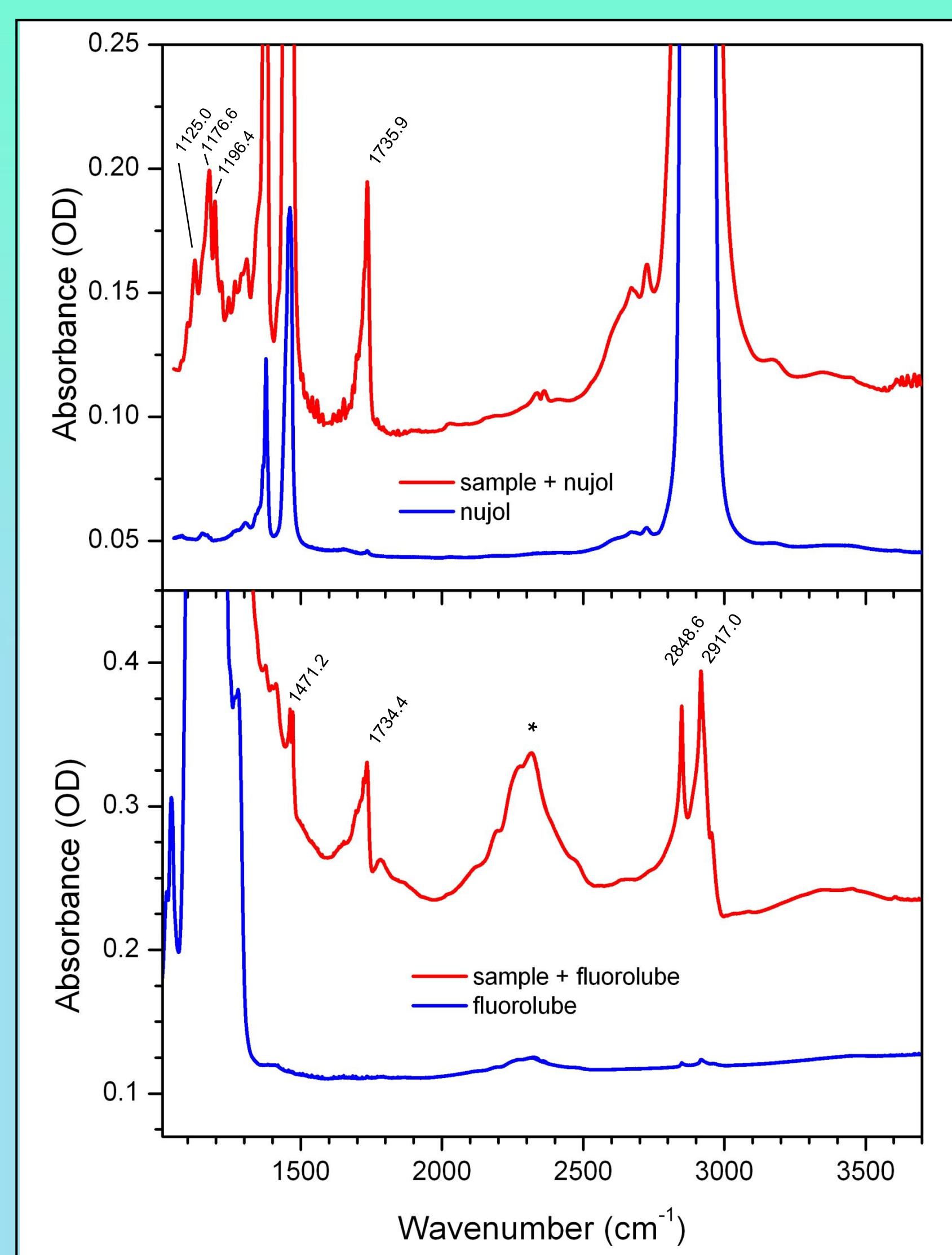


Fig. 2 FTIR spectra of sample prepared with Nujol (top) and Fluorolube (bottom). The peak marked (*) is an overtone band of Fluorolube.

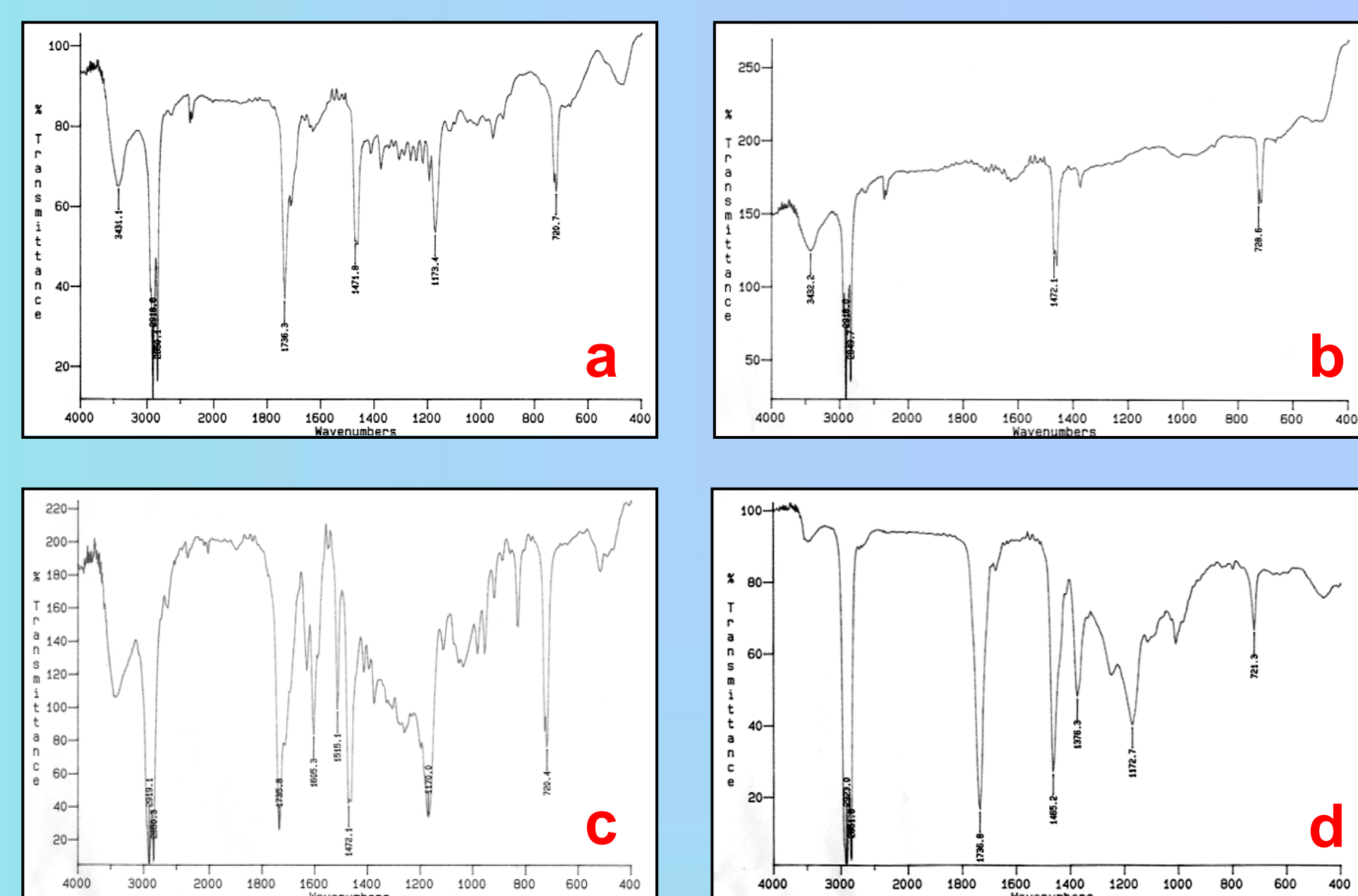


Fig. 3 FTIR spectra of a) beeswax,³ b) paraffin wax,⁴ c) carnauba wax,⁵ and d) lanolin.⁶

Results – ¹H-NMR

Figure 4 shows the ¹H-NMR spectrum of the sample, which exhibits five main peaks at: 4.062, 2.296, 1.620, 1.261, and 0.888 ppm. The triplets at 4.062 and 2.296 are diagnostic for methylene groups bound to the O- and carbonyl moieties of an ester group, respectively, while the very strong peak at 1.261 indicates the presence of a long hydrocarbon chain. Finally, the peak at 1.620 ppm represents connector CH₂ groups linking the hydrocarbon chains to the methylenes bound to the ester. Peak integrations (shown in red on figure 4) are consistent with an overall chain length of 40-45 methylene groups. Note also the strong similarity of the sample spectrum with the reference spectrum of butyl palmitate shown in Figure 5. Although there are some weak bands indicating low levels of other molecules, the strong signal and sharp peaks (see insets a, b) in Figure 4 indicate that the sample consists primarily of one or more chemically similar, long chain esters, such as palmitate. This is again indicative of a natural wax; for example, beeswax consists largely of myricyl palmitate, CH₃(CH₂)₂₉OC=O(CH₂)₁₄CH₃,⁷ which is consistent with both the peak shifts and the estimates of chain length from peak integration data. The 2D COSY-NMR spectrum shown in Figure 6 provides further corroboration of this assignment, since it clearly shows that the methylene groups at 1.620 ppm are coupled to both the ester peaks at 4.062 and 2.296 ppm, and the large peak at 1.261 ppm, while the latter peaks are not coupled.

¹H-NMR Spectra

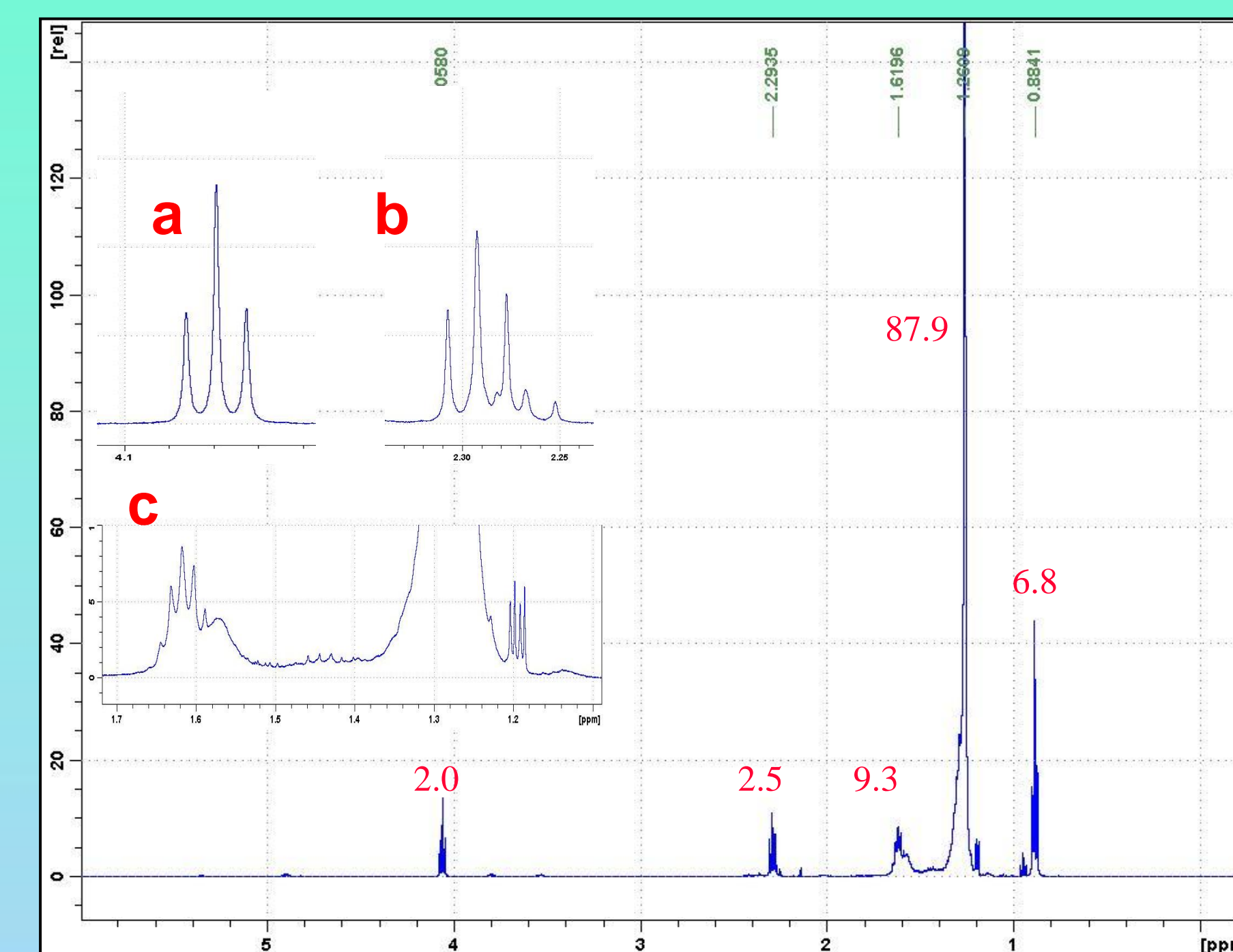


Fig. 4 ¹H-NMR spectrum of sample w/ peak integrations (red #'s) normalized to ester CH₂ @ 4.062 ppm. Insets: Close-ups of ester peaks at a) 4.062 ppm b) 2.296 ppm c) 1.26 ppm

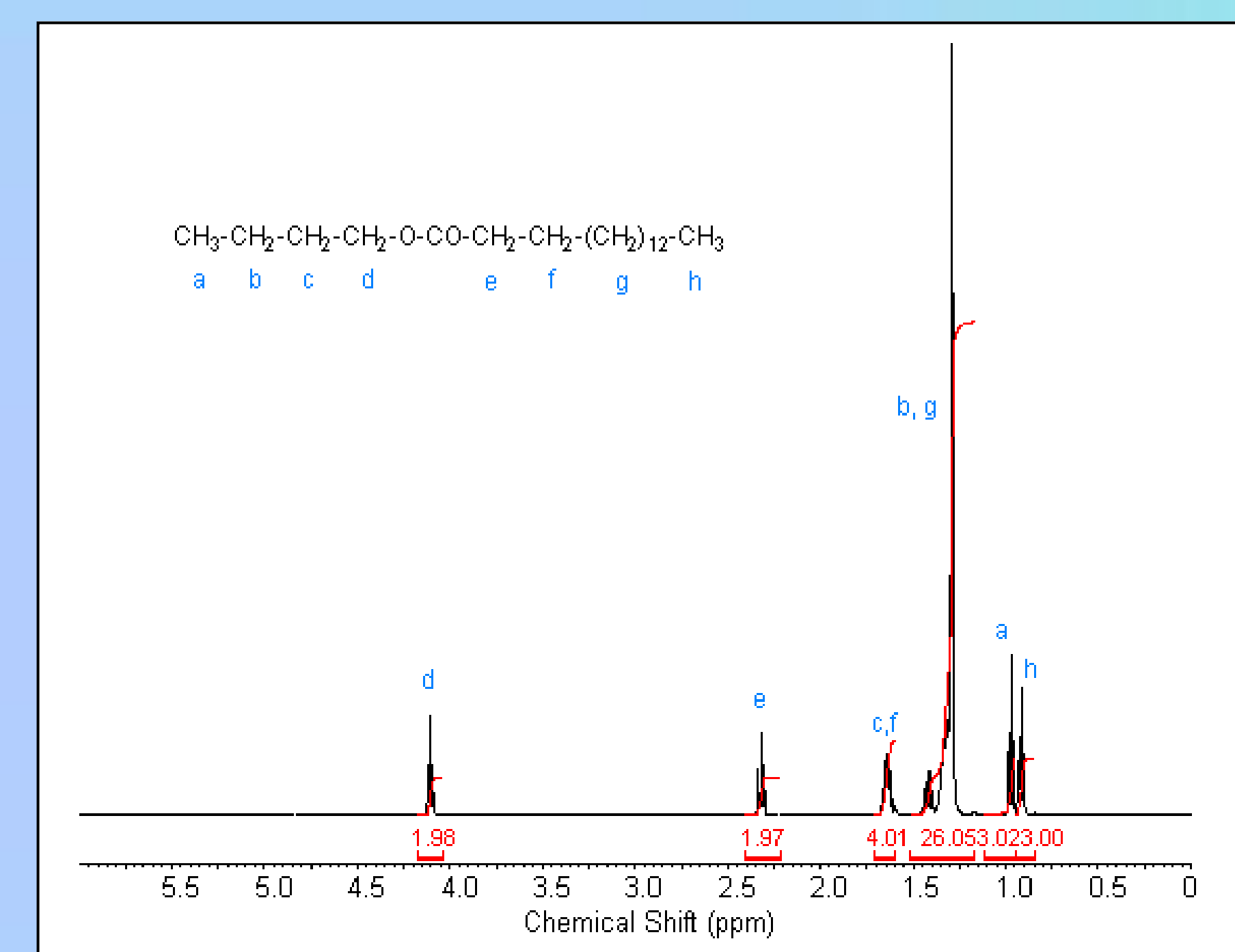


Fig. 5 ¹H-NMR Spectrum of butyl palmitate with peaks assigned².

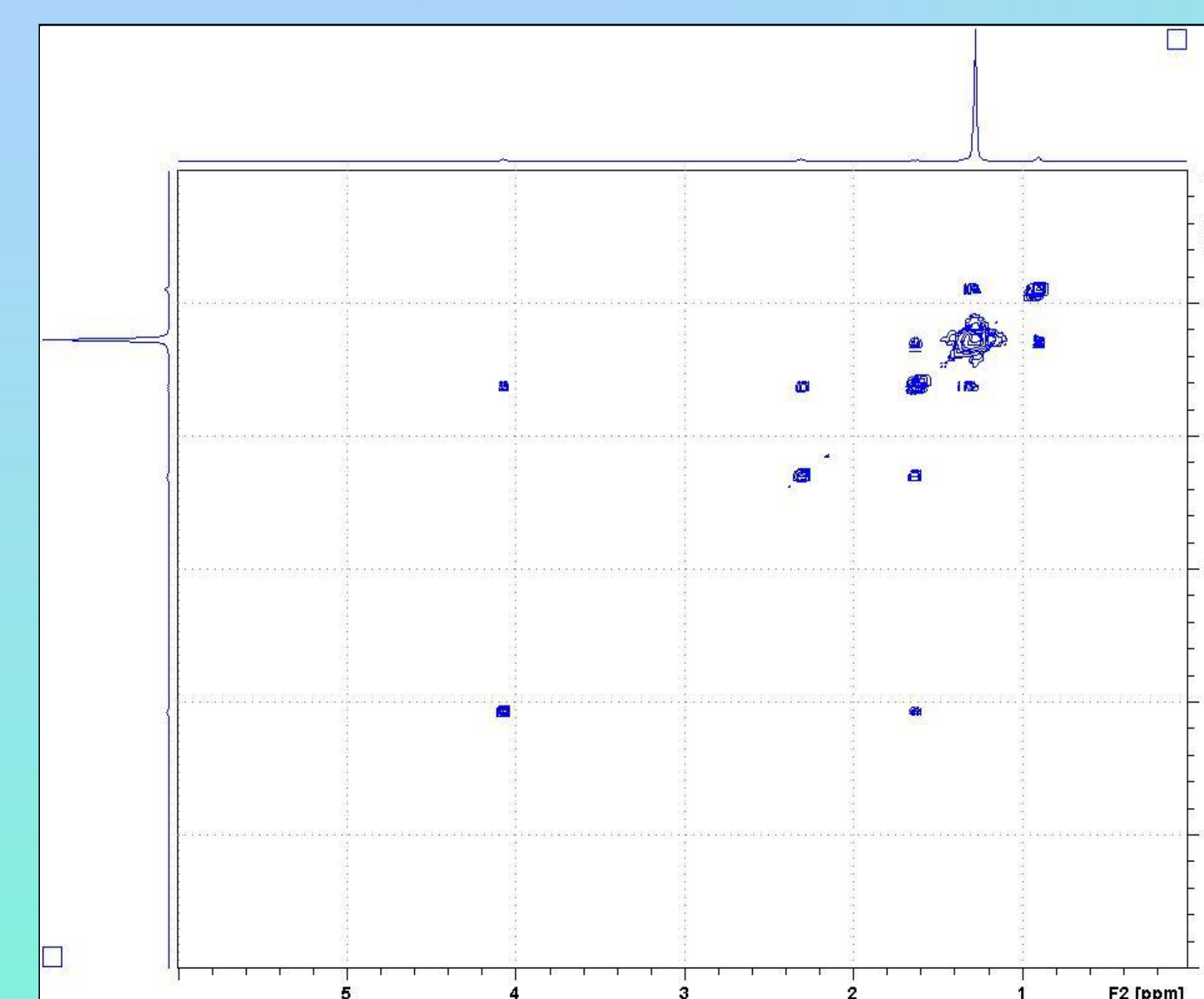


Fig. 6 2D COSY-NMR spectrum of sample

Results – ¹³C-NMR

Figure 7 shows the ¹³C-NMR spectrum of the sample, and is consistent with a long-chain ester, supporting the conclusions drawn above. The large peak at 30 corresponds to that of the hydrocarbon chain, while that at 64 represents the carbon bound to the oxygen of an ester.⁸ There is also a weak carbonyl peak at ~174 ppm (see inset). More importantly, comparison with the reference ¹³C-NMR spectra of beeswax and lanolin (Figs. 8a and b, respectively), provides near conclusive identification of the sample as beeswax. It can be easily seen that the lanolin spectrum contains numerous peaks that are not seen in Fig. 7, while the beeswax spectrum very closely resembles that of our sample.

¹³C-NMR Spectra

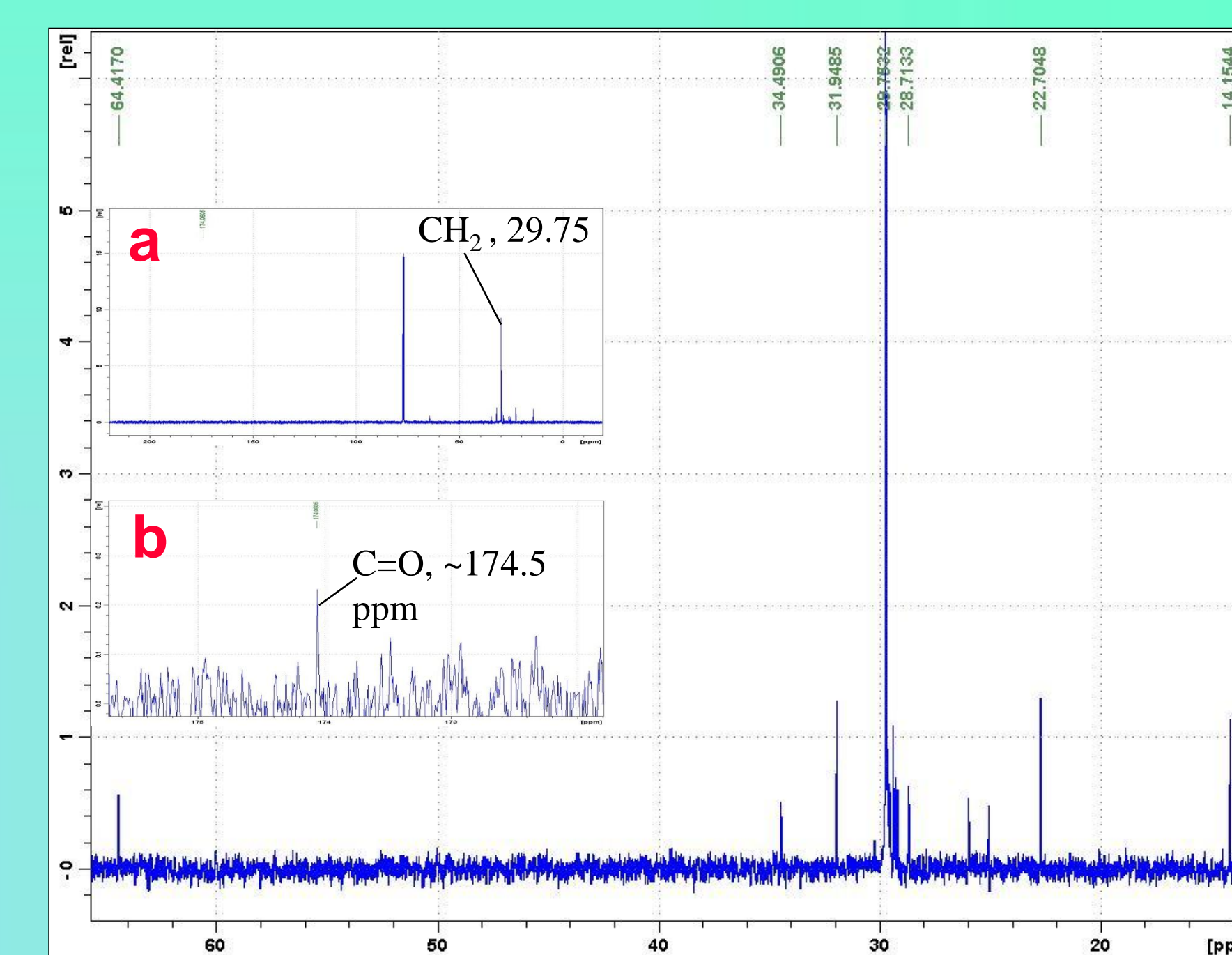


Fig. 7 ¹³C-NMR Spectrum of sample. Insets: a) overall spectrum, b) C=O peak

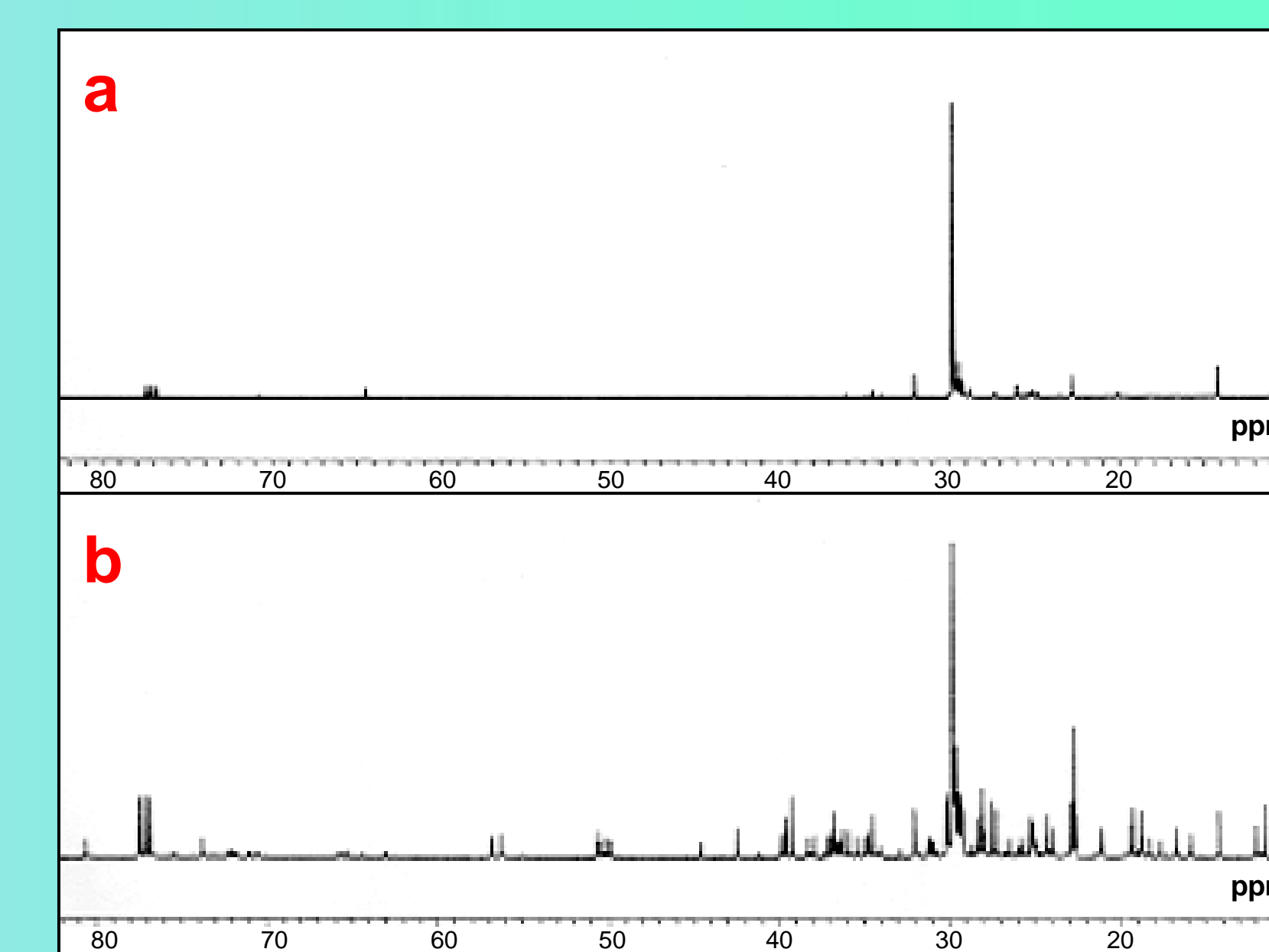


Fig. 8 ¹³C-NMR Spectra of a) beeswax³ and b) lanolin wax.⁶

Conclusions and Future Work

The FTIR and ¹H-NMR data indicate that the principal component (> 80%) of the unknown substance is a long-chain ester, which is consistent with the substance being an animal wax, such as beeswax or lanolin wax. The ¹³C-NMR data further narrow the identification to beeswax, based on comparison with reference spectra from the literature.³ It should be noted that other animal waxes, for which reference spectra could not be found, are also possibilities. For example, spermaceti wax and Chinese insect wax each have a long chain ester as their principal component (cetyl palmitate and ceryl cerotate, respectively), although the melting points do not match (42-50 and 82-84 C, respectively).⁷

Planned future work includes more in-depth NMR and mass spectrometric analysis to identify trace components, which could help narrow the geographic origin of the wax. For example, Asian beeswax has trace amounts of glycerides not found in European beeswax.³ Furthermore, since a clear chain of custody for this artifact has not been established, it will ultimately be necessary to chemically date the sample using ¹⁴C-dating.

Acknowledgements

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