

# SYNTHESIS OF ETHYL FATTY ALKYL ETHERS FROM COCONUT (*Cocos nucifera* L.) FATTY ALCOHOLS

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## ABSTRACT

Ethyl fatty alkyl ethers were synthesized using coconut fatty alcohols as the starting raw materials. The fatty alcohols were converted into their corresponding bromides which were then made to react with ethanolic potassium hydroxide. The average percent yield of ethyl fatty alkyl ethers was 74.30%. The products were characterized using chemical tests, infrared (*ir*) spectrophotometry, and proton magnetic resonance (*pmr*) spectroscopy.

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**KEY WORDS:** Ethyl fatty alkyl ethers. Coconut fatty alcohols. *Cocos nucifera* L.

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## INTRODUCTION

Coconut oil is an important export product of the Philippines with varied uses. Its chemical composition and unique characteristics render it suitable for a number of edible and non-edible preparations. These unique characteristics should be put into good use especially since

the country's export earnings from coconut has markedly dropped for almost a decade now. This drop could be attributed to the presence of coconut oil competitors in the world market like oil derived from soybean, cottonseed, palm kernel and babassu-kernel (Thieme, 1968; Child, 1974) as well as cuphea (Kern, 1979). American chemists,



for example, have improved soybean oil so successfully that it has now completely replaced coconut oil in the American market (Banzon, 1986).

With the expected increase in coconut production and the decrease in demand for coconut products in the world market, it is essential that the utilization of these products in the manufacture of coco-based chemicals must be intensified. Bowers and Thompson (1963), Krishnakumaran and Schneiderman (1965), and Bryant and Sang (1969) described some coco-based ethers having potential insecticidal properties. This study was thus conducted to synthesize ethyl fatty alkyl ethers from coconut fatty alcohols, the products of reduction of fatty acids. Considering the fact that industrial-scale production of fatty alcohols is already existing in the country, it would likely be economical to start from fatty alcohols rather than from coconut oil in the synthesis.

## MATERIALS AND METHODS

The coconut fatty alcohols were bought from Coco-Chemical Philippines, Inc. in Cotta, Lucena City. The preparation of fatty alkyl ethers from coconut fatty alcohols involved two steps. The first step was the alkylation of the coconut fatty alcohols to their halides with the use of hydrobromic acid and sulfuric acid. The second step was the transformation of the prepared fatty

alkyl halides to fatty alkyl ethers with the use of potassium ethoxide. The detailed procedure is described below.

### *Preparation of Constant-Boiling Hydrobromic Acid*

Constant-boiling hydrobromic acid (48%) was prepared using the method described by Vogel (1956). In a 1-L flask, 240 g of potassium bromide was dissolved in 400 mL water. The solution was cooled in an ice bath and 180 mL of concentrated sulfuric acid was slowly added. The temperature was not allowed to rise above 75°C to prevent the formation of bromine. The resulting solution was cooled to room temperature and distilled. The fraction which boiled at 124-127°C was collected.

### *Preparation of Fatty Alkyl Bromides*

The method used by Kamm and Marvel (1961) and Rodriguez (1980) was modified to prepare alkyl bromides from coconut fatty alcohols. Seventy grams (0.42 mole) of 48% hydrobromic acid and 22 g (12 mL) of concentrated sulfuric acid were placed in a 250-mL round-bottom flask. Forty-one grams (0.22 mole, computation based on lauryl alcohol) of coconut fatty alcohols was added. The mixture was refluxed for 12 hours or longer using a hot plate-magnetic stirrer. The final reaction mixture was then diluted



with water. The organic layer was separated and carefully washed with cold concentrated sulfuric acid. Enough 50% methyl alcohol and aqueous ammonia were added to the crude organic product until the mixture was basic. This was done to remove alkyl hydrogen sulfate present which could cause the formation of troublesome emulsions in the succeeding steps (Blatt, 1959; Rodriguez, 1980). The crude organic product was separated and washed with water followed by dilute sodium carbonate, and dried with anhydrous calcium carbonate. The anhydrous organic product was then distilled at 100-210°C under reduced pressure (90-100 mm Hg).

#### *Reaction of Fatty Alkyl Bromides with Ethanolic Potassium Hydroxide*

Ethyl fatty alkyl ethers were synthesized using the procedure described by Roberts et al. (1969) and Rodriguez (1980) with modifications. In a 250-mL round-bottom flask, 8.4 g (0.150 mole) of potassium hydroxide and 53 mL of absolute ethanol were placed. The mixture was heated in a reflux condenser until all the potassium hydroxide had dissolved. The solution was cooled in a water bath, then 18.68 g (0.075 mole, computation based on lauryl bromide) of alkyl bromides was added. The mixture was refluxed for 7 hours or longer and the final reaction mixture was then poured into 200 mL of ice-cold

water. The separated organic layer was extracted, washed with water, and dried with anhydrous magnesium sulfate. The crude organic product was distilled at 100-210°C under reduced pressure (90-100 mm Hg).

#### *Characterization of Fatty Alkyl Bromides and Ethyl Fatty Alkyl Ethers*

The resulting products were characterized using chemical tests (Vogel, 1956; Rodriguez, 1980), infrared (*ir*) spectrophotometry, and proton magnetic resonance (*pmr*) spectroscopy. The changes in the molecular structures of the compounds from alcohol to halide, then to ether were traced out from the resulting spectra and chemical tests.

## RESULTS AND DISCUSSION

#### *Fatty Alkyl Bromides from Coconut Fatty Alcohols*

The preparation of fatty alkyl bromides involved the conversion of coconut fatty alcohols to alkyl sulfates with the use of concentrated sulfuric acid and the displacement of the hydrogen sulfate group by bromine. Purification of the product by distillation under reduced pressure yielded a colorless liquid with a foul smell. The liquid turned light yellow upon standing at room temperature. According to McCullough and Cortese (1929),



halides prepared with the aid of sulfuric acid tend to spoil more easily and develop colors on keeping. Sulfuric acid splits out halogen acid forming small quantities of olefins which polymerize to produce colored products.

The average yield of fatty alkyl bromides was 68.36% (density, 1.0158 g/mL) although yield as high as 74.65% was obtained. An average of 0.91 g of fatty alkyl bromides was produced per gram of the fatty alcohols. Lauryl bromide was made as the basis for computation because it is the alkyl bromide derived from lauryl alcohol, the major component of coconut fatty alcohols.

Chemical tests showed the presence of bromine atom in the molecule and the almost complete transformation of fatty alcohols into alkyl bromides. The results of *ir* spectrophotometry of the fatty alcohols and fatty alkyl bromides agreed with the chemical tests. Figure 1 shows the *ir* spectrum of the fatty alcohols. The broad absorption at  $3340\text{ cm}^{-1}$  and  $1054\text{ cm}^{-1}$  are characteristics of the stretching vibrations of the O-H and C-O asymmetric stretching vibrations of primary alcohols, respectively, affected by intermolecular hydrogen bonding (Silverstein et al., 1981). The disappearance of these absorptions in the *ir* spectrum of alkyl bromides (Fig. 2) and the appearance of absorptions at  $1250\text{ cm}^{-1}$  and  $640\text{ cm}^{-1}$  which are due to the C-H wagging vibrations of the  $-\text{CH}_2\text{-Br}$

group and C-Br stretching vibrations, respectively, support the conversion of the fatty alcohols to fatty alkyl bromides.

The *pmr* spectrum of fatty alkyl bromides is shown in Figure 3. The deshielding effect of the bromine atom on the methylene directly attached to it shifted the absorption peak downfield to  $3.43\delta$ , which is a triplet. It also affected the  $\beta$ -protons which gave a broadened multiplet at  $1.80\delta$  (Silverstein et al., 1981). The rest of the methylene protons in the fatty alkyl chain which are of the same chemical environment gave a broadened singlet at  $1.25\delta$ . The methyl protons gave a deformed triplet at  $0.86\delta$ . It is observed as a deformed triplet because the product sample was a mixture of alkyl bromides.

#### *Ethyl Fatty Alkyl Ethers from Fatty Alkyl Bromides and Ethanolic Potassium Hydroxide*

The average yield of ethyl fatty alkyl ethers from fatty alkyl bromides and ethanolic potassium hydroxide was 74.30% (density, 0.8322 g/mL), which means that 0.64 g of product was obtained per gram of fatty alkyl bromides. Purification by distillation at 90-100 mm Hg gave a clear and colorless liquid which was less viscous than that from the fatty alcohols. Chemical tests showed no reaction with hot, dilute, neutral potassium permanganate and with alcoholic silver



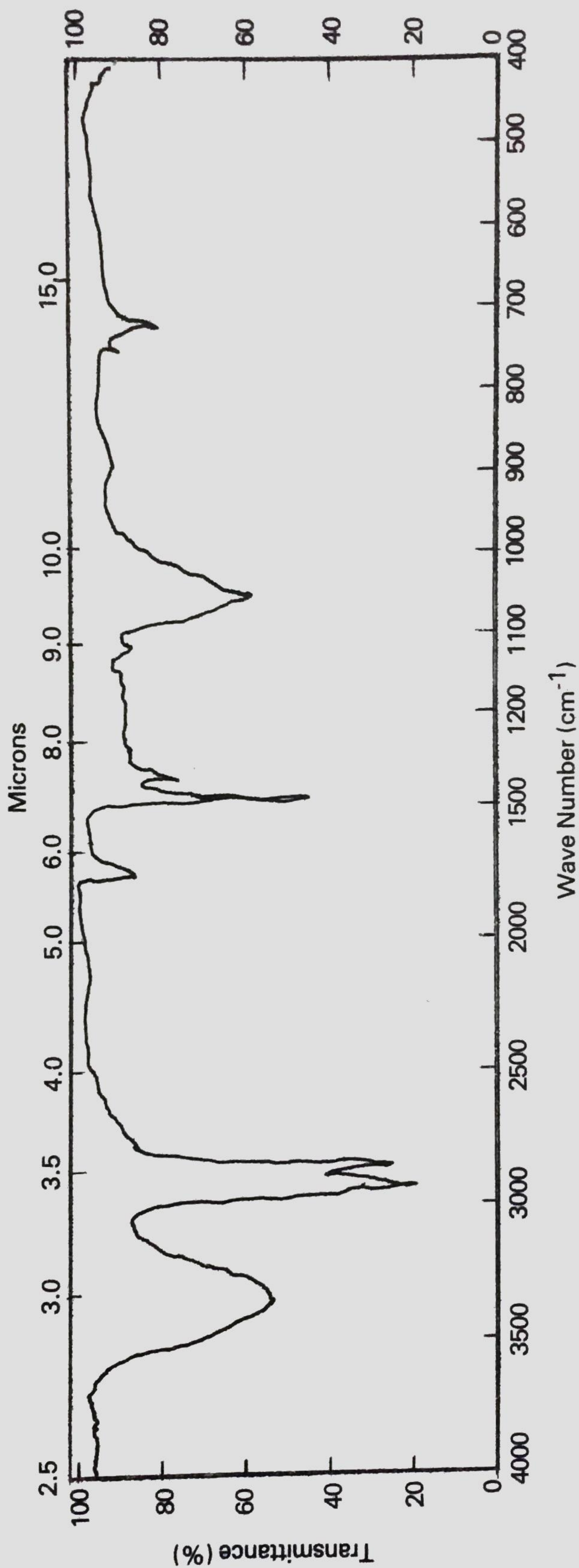


Figure 1. Infrared spectrum of coconut fatty alcohols.



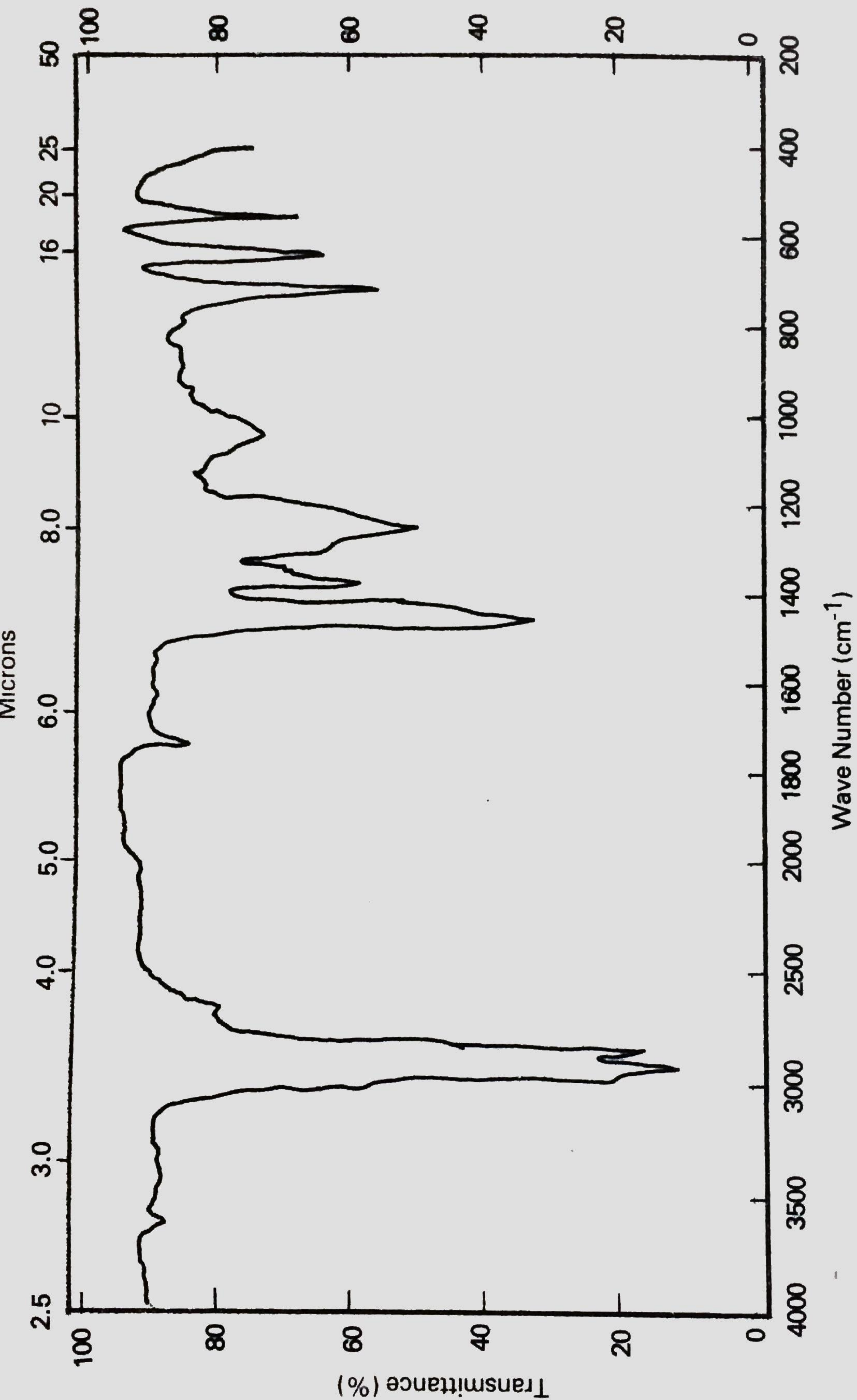


Figure 2. Infrared spectrum of alkyl bromides prepared from coconut fatty alcohols and 48% hydrobromic acid.



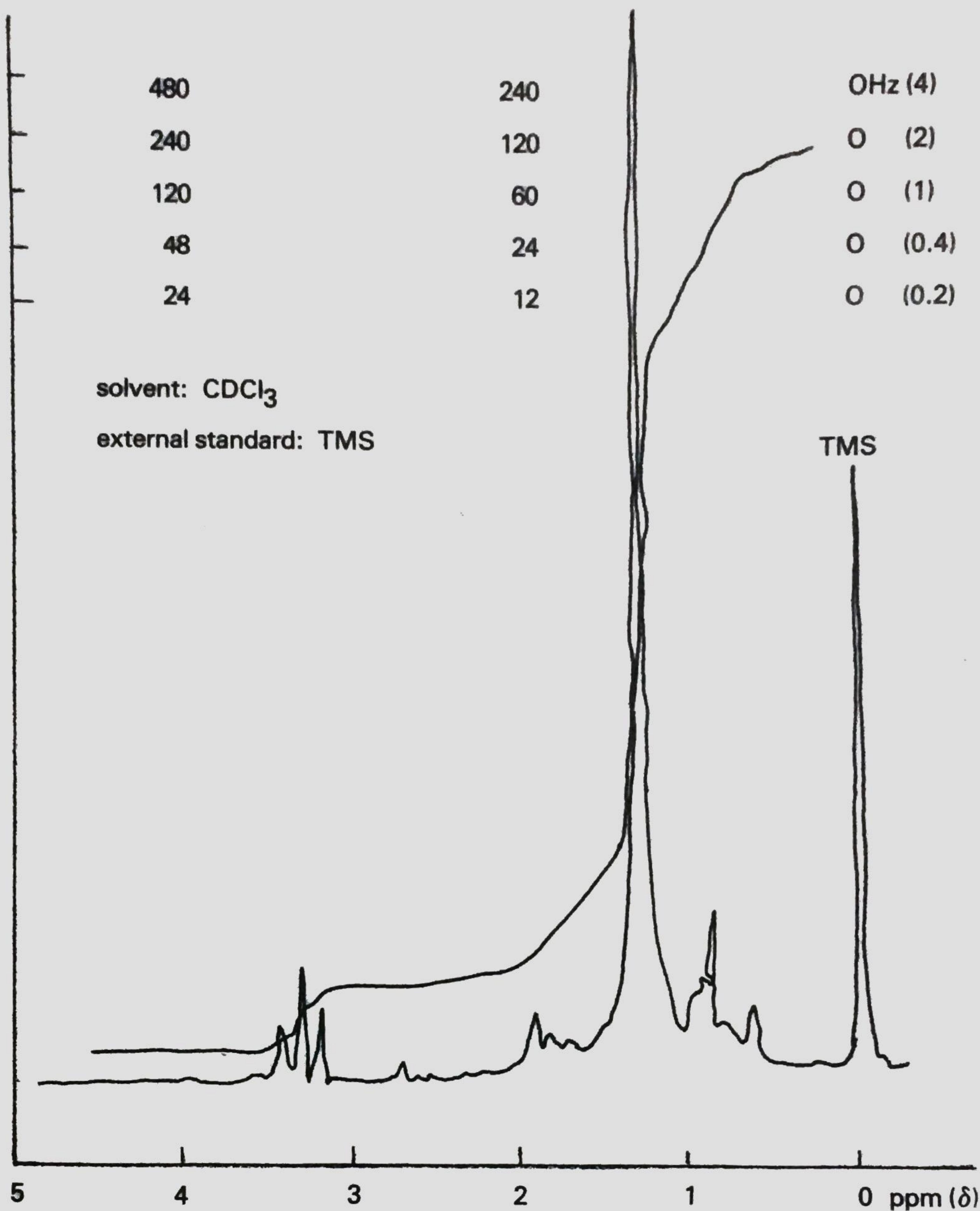


Figure 3. Proton magnetic resonance spectrum of alkyl bromides prepared from coconut fatty alcohols and 48% hydrobromic acid (60 MHz).



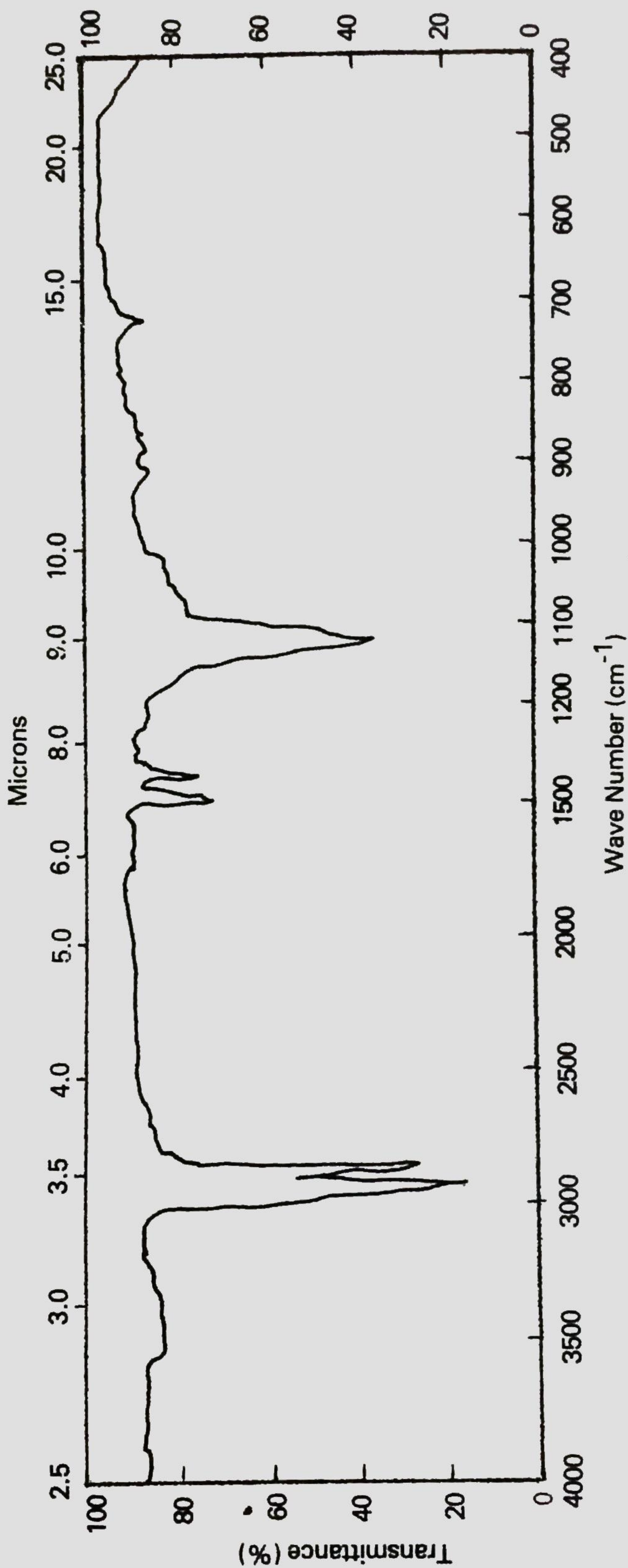


Figure 4. Infrared spectrum of ethyl fatty alkyl ethers prepared from alkyl bromides and ethanolic potassium hydroxide.



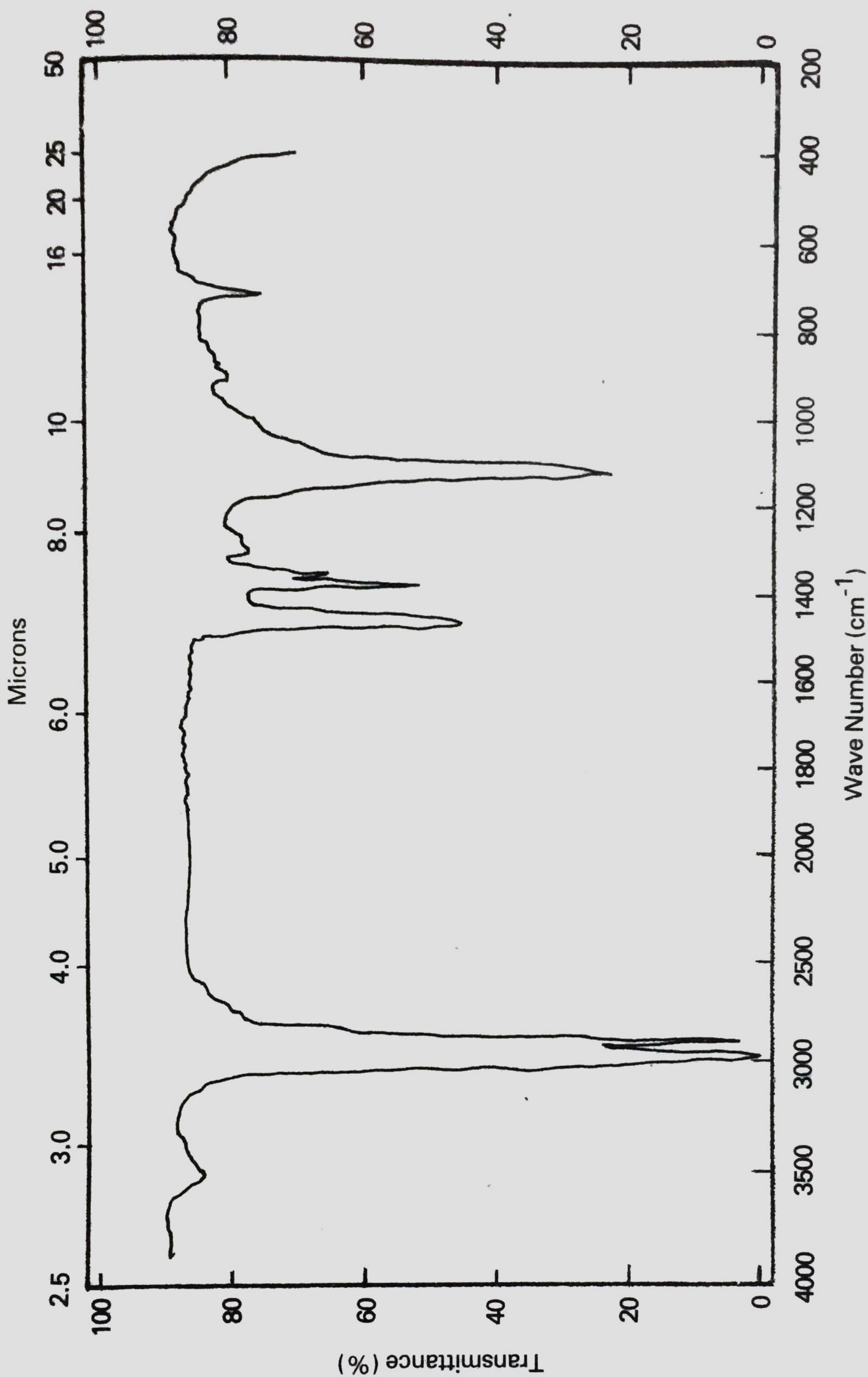
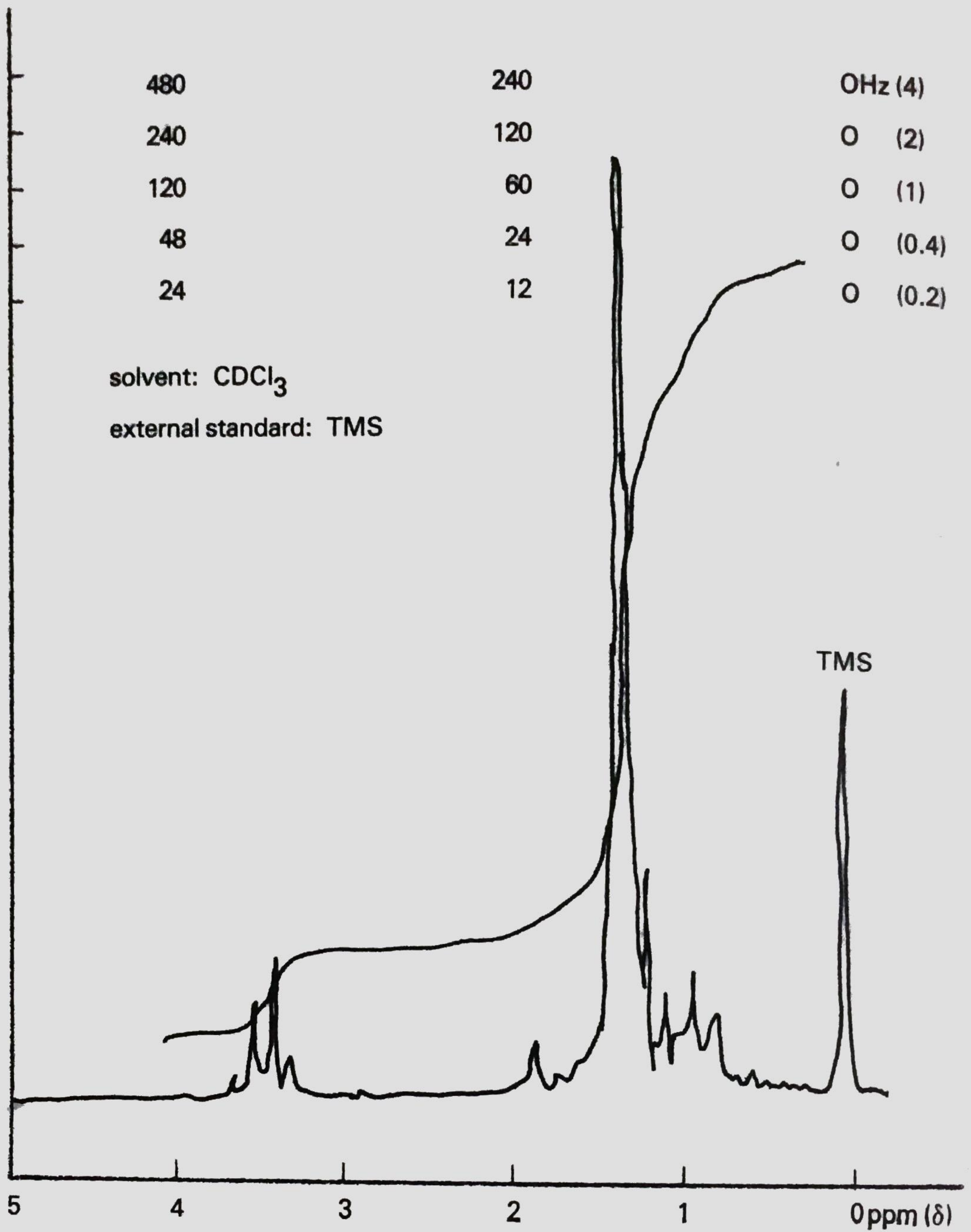


Figure 5. Infrared spectrum of ethyl lauryl ether synthesized from lauryl bromide and sodium ethoxide.





**Figure 6.** Proton magnetic resonance spectrum of ethyl fatty alkyl ethers prepared from alkyl bromides and ethanolic potassium hydroxide (60 MHz).



nitrate suggesting the absence of unreacted ethanol and fatty alkyl bromides, respectively.

The *ir* spectrum of the product (Fig. 4) shows an absorption at  $1120\text{ cm}^{-1}$  which is caused by -C-O-C asymmetrical stretching vibration in aliphatic ethers. The absorptions at  $2930\text{ cm}^{-1}$ ,  $2860\text{ cm}^{-1}$ ,  $1470\text{ cm}^{-1}$ ,  $1380\text{ cm}^{-1}$ , and  $720\text{ cm}^{-1}$  are also found in the *ir* spectra of fatty alcohols and fatty alkyl bromides (Figs. 1 and 2) indicating the presence of the same hydrocarbon chain. The disappearance of the O-H and C-Br absorptions in this spectrum proves the complete conversion of the reactants into ethyl fatty alkyl ethers. Similar results were observed in the *ir* spectrum of ethyl lauryl ether (Fig. 5) using lauryl alcohol.

The *pmr* spectrum of the ethyl fatty ethers (Fig. 6) shows a triplet at  $0.88\delta$  which is due to the protons of the methyl group of the ethyl moiety

and of the fatty alkyl chain. The broadened singlet at  $1.26\delta$  is attributed to the methylene protons in the fatty alkyl chain. The relatively greater area of this particular peak indicates that the methylene protons with the same chemical environment are greater in number suggesting the presence of long saturated hydrocarbon chain. The distorted multiplet at  $1.70\delta$  is due to the methylene protons near the oxygen atom or the  $\beta$ -protons. The deformed triplet at  $3.24\delta$  is due to the methylene protons of the fatty alkyl chain that is directly attached to the oxygen atom or the  $\alpha$ -protons. The methylene protons of the ethyl group that is directly attached to the oxygen caused a quartet at  $3.45\delta$ . The  $\alpha$ -protons are the most deshielded protons in the molecule due to the electronegativity of the oxygen atom, thus they are detected at a lower field.

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