# Synthesis of Jojobamide and Homojojobamide

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## ABSTRACT

Jojobamide has been synthesized from methyl jojoboate (the transesterification product of jojoba oil and methanol) and concentrated ammonium hydroxide by high temperature treatment of the mixture in a sealed vessel. Homojojobamide has been synthesized by partial hydrolysis of homojojobylnitrile, which was prepared from jojobyl mesylate. The melting points of the amides were found to be relatively high (>75 C) for a mixture of amides.

## INTRODUCTION

Amides of long chain aliphatic acids are known for their useful chemical and physical-technological properties (1), and thus it is of interest to prepare the amides which are derived from the acids, which form the esters of jojoba oil. These acids are mainly (*Z*)-11-eicosenoic acid (70%), (*Z*)-13-docosenoic acid (erucic acid) (14%), and (*Z*)-9-octadecenoic acid (oleic acid) (10%) (Table I). Oleamide and erucamide are important additives in the polymer processing industry (1). It is interesting to study the properties of jojobamide and its higher homologue homojojobamide. We, therefore, looked for simple and efficient syntheses of jojobamide (IV) and homojojobamide (VII) in order to supply these products for different tests.

## EXPERIMENTAL PROCEDURES

### General

Crude jojoba oil was purified by mixing it with bleaching earth at 60 C for 30 min and then filtering under vacuum. The crude product after each chemical transformation was used without further purification for the next step. The usual workup consisted of pouring the reaction mixture into $H_2O$, extraction with petroleum ether (60-80), washing with saturated NaCl solution, and drying over anhydrous $Na_2SO_4$. IR and NMR spectra provided monitors for the chemical change occurring in each reaction. Purity was determined by NMR as described later. All NMR spectra gave the following: terminal $CH_3$ as triplet at $\delta$ 0.92-0.94; an intense signal at 1.2-1.4 for all aliphatic hydrogens; a signal at 1.98-2.05 for allylic hydrogens; and a quintet at 5.20 (J=5 cps) for the olefinic hydrogens. Other signals are summarized in Table II. Integration curves were consistent for the assignment of the different hydrogens. All the reactions were followed by NMR using the $-CH_2-Y$ group signal to identify the components of the mixture and to calculate its exact composition (±2% of absolute amount). This analytical procedure was confirmed by preparing known mixtures, using small amounts of "impurities" of one or two components; these could be detected in amounts as little as 2-3% of the mixture. This method was found to be fast, easy, reliable, reproducible, and sufficiently sensitive for practical and even semiquantitative work. In general, the reaction was continued until complete transformation took place as determined by NMR.

TABLE I

Percentage of Products from Hydrolysis and Reduction of Jojoba Oil (1)[a]

| | $C_{18}$ | $C_{20}$ | $C_{22}$ | $C_{24}$ | Total |
|---|---|---|---|---|---|
| | | Hydrolysis | | | |
| (m) = | (7) 10-11 | (9) 70-71 | (11) 13-15 | (13) 2-3 | 95- |
| (n) = | (8) 1-2 | (10) 45-46 | (12) 42-43 | (14) 7-8 | 95- |
| | | Reduction | | | |
| (p) = | (8) 5-6 | (10) 57-58 | (12) 27-29 | (14) 5-6 | 94- |

[a]Ref. 3 and Scheme 1.

TABLE II

Chemical Shifts of α-Methylene (t, J=6 cps) in Different Long Chain Derivatives

$(Z)\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_x\underline{CH_2}Y$

| Y | OMes | $\overset{O}{\overset{\|}{\text{OCR}}}$ | OH | $\overset{O}{\overset{\|}{\text{COCH}_3}}$ | CN | $\overset{O}{\overset{\|}{\text{CNH}_2}}$ |
|---|---|---|---|---|---|---|
| $\delta$[a] | 4.10 | 3.95 | 3.45 | 2.26 | 2.24 | 2.20 |

[a]$\delta$, ppm downfield from TMS as internal standard in $CCl_4$ solution.

IR was also used for monitoring the reaction of methyl jojoboate with $NH_4OH$ by plotting the ratio of absorption intensity of the two carbonyls in the reaction mixture (amide and ester) versus concentration. The line obtained was a less accurate determination than NMR monitoring. The correlation between the IR and NMR measurements is shown in Figure 1, which gives a relatively straight line. The fact that the line does not start at the origin might stem from the measuring of line absorption intensity rather than its total area.

The NMR spectra were determined on a Varian XL-100, in $CCl_4$ or $CDCl_3$ solution. The IR spectra were determined with a Perkin Elmer 377 usually neat or in $CHCl_3$ solution.

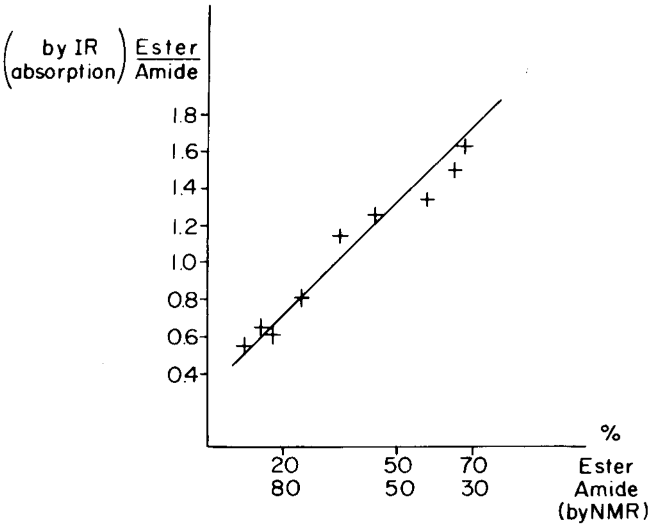


FIG. 1. IR vs. NMR correlation for amide formation at 190 C.

TABLE III

Effect of Temperature on Jojobamide Formation

| Bath t C | Hours | Methyl ester and alcohol (g) | $NH_4OH$ 25-28% (ml) | Amide yield |
|---|---|---|---|---|
| 60 | 24 | 30 (0.05 mol ester) | 20 (0.14 mol) | — |
| 90 | 48 | 30 (0.05 mol ester) | 20 (0.14 mol) | — |
| 130 | 12 | 30 (0.05 mol ester) | 25 (0.18 mol) | 25%-30% |
| 150 | 24 | 30 (0.05 mol ester) | 25 (0.18 mol) | 35%-40% |
| 150 | 48 | 30 (0.05 mol ester) | 50 (0.36 mol) | 88%-90% |
| 150 | 24 | 30 (0.05 mol ester) | 100 (0.72 mol) | 40%-43% |
| 190 | 4 | 30 (0.05 mol ester) | 50 (0.36 mol) | 53%-55% |
| 190 | 9 | 30 (0.05 mol ester) | 50 (0.36 mol) | 68%-70% |
| 190 | 13 | 30 (0.05 mol ester) | 50 (0.36 mol) | 79%-81% |
| 190 | 24 | 30 (0.05 mol ester) | 50 (0.36 mol) | 94%-96% |

### Solvents

Petroleum ether (60-80) was dried over $CaCl_2$ and distilled. Ether was dried over $CaCl_2$, then over Na and distilled. Pyridine was kept over KOH prior to its use. Methanol, benzene, toluene, DMSO, and t-BuOH all were CP and used without drying.

### Transesterification of Jojoba Oil (I) to Methyl Jojoboate (III)

Two liters of methanol were cooled in an ice-salt-water bath and 120 ml acetyl chloride (109 g, 1.6 mol) added dropwise so that the inside temperature was kept below 5 C. The addition took 1½ hr. This solution was then added to 212 g of jojoba oil (0.36 mol) in 200 ml benzene and refluxed for 4 hr. On cooling it was poured into 3 liters of water. The organic phase separated, and the aqueous phase was extracted with petroleum ether. The organic phases were combined, washed with $NaHCO_3$ solution, saturated NaCl solution, and dried over $Na_2SO_4$. Evaporation of the solvent left 226 g of a mixture of methyl jojoboate (97%) and jojobyl alcohol (IIb) in 1:1 ratio. IR 1740 $cm^{-1}$.

### Amidation of Methyl Jojoboate (III) to Jojobamide (IV)

The reaction was carried out in a sealed steel reactor lined with Teflon that was heated in a wax bath to the desired temperature (Table III and Fig. 2). At the end of the reaction, the aqueous phase was decanted. The remaining solid was dissolved in chloroform, evaporated to dryness, and then evaporated with 2 portions of toluene to remove traces of water. The semisolid product was centrifuged. The upper layer, composed mainly of alcohols with traces of unreacted methyl ester and small amount of amide, was then removed. The residue was triturated with cold petroleum ether and centrifuged again. This procedure could be repeated until maximum purity was obtained. Usually, one trituration was sufficient to obtain technical grade amide. MP is in the range of 75-85 C, depending on the purity of the amide. IR 1680 $cm^{-1}$.

### Homojojobylnitrile (VI)

To a solution of 14.7 g of NaCN (0.3 mol) in 200 ml warm DMSO (85-90 C), 80 g of mesylate (V) (0.2 mol) was added dropwise while the temperature was kept at 85-100 C. After stirring for 3 days at 90-100 C and regular workup, 63 g of VI (96%) was isolated. IR 2225 $cm^{-1}$. $n_D^{26.5}$ 1.4592. Calcd. for N, 4.54%; found 4.2%.

### Hydrolysis of Homojojobylnitrile (VI) to Homojojobamide (VII)

A mixture of 86.2 g homojojobylnitrile (0.29 mol) and 140 g KOH (2.5 mol) in 600 ml *t*-BuOH was mechanically stirred and refluxed for 2½ hr (not all the KOH dissolved). On cooling, it was poured into 1-liter saturated NaCl solution. The amide floated to the top and was extracted with chloroform, dried, and evaporated to yield 86.4 homojojobamide (92%). The amide was purified by trituration with petroleum ether, mp 75-85 C.

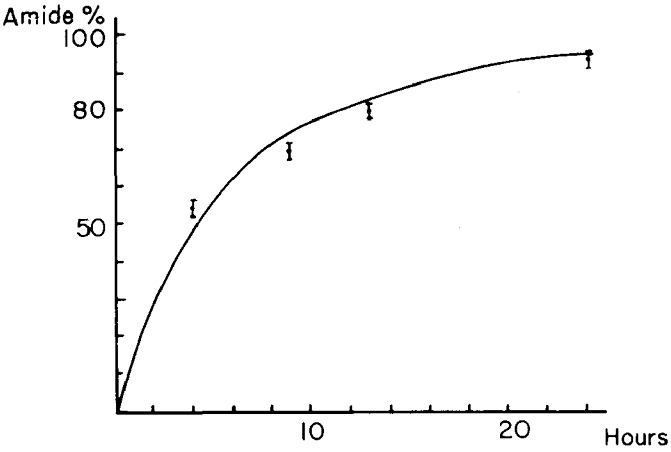
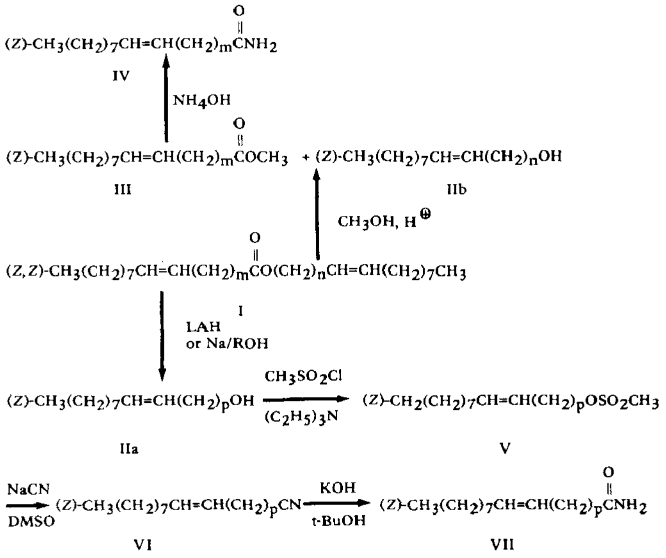


FIG. 2. Percent amide formation with time at 190 C.

## RESULTS AND DISCUSSION

Jojoba oil is a mixture of esters, composed of long chain acids and alcohols (Table I) (2). The easiest and most straightforward synthesis of an amide from an ester is by applying concentrated $NH_4OH$ to the ester for a period of time, after which the amide separates as a solid product. This procedure was found to give negative results with jojoba oil both at room temperature and at elevated temperature and high pressure. This behavior can be explained by the oily character of the ester and because of steric interference which resulted from its long chains on both sides of the carbonyl group. Thus, by replacing the alcoholic chain with a short one, like methyl, one can obtain a much better system for amide formation (Scheme 1). Transesterification of jojoba oil with methanol yields quantitative conversion to 1:1 mixture of methyl jojoboate (methyl esters of jojoba acids) III and jojoba alcohol IIb. This mixture is then submitted to rather more drastic conditions than are usual for amidation of esters, to yield a semisolid product, which contains jojoba alcohol in ca. 50% of the weight, 45-48% of jojobamide and 2-5% of methyl jojoboate (90-95% conversion). Effect of temperature and reaction time on amide formation is given in Table III and



m = 7,9,11,13
n* = 8,10,12,14
p* = 8,10,12,14

**SCHEME 1. *In different composition, see Table I.**

Figure 2. The amide was purified from the accompanied jojoba alcohol, which could be used for other preparations and syntheses of jojoba products.

Elongation of the jojoba chain is achieved by converting jojoba mesylate V (4) to the nitrile VI (A. Shani and E. Horowitz, unpublished results), which contains one more carbon atoms to form the next homologue. This nitrile is hydrolyzed (5) to homojojobamide VII in high yield (Scheme 1). The overall yield is 70% starting from the oil I.

It is interesting to note that jojobamide and homojojobamide differ both in their chain length and in composition (Table I). Thus, jojobamide is derived mainly from eicosenoic acid (70%), erucic acid (14%), and oleic acid (10%); while homojojobamide is a mixture of $C_{19}$:$C_{21}$:$C_{23}$:$C_{25}$ amides in the ratio of 1:10-11:5-6:1, respectively. These two factors might contribute to different physical and technological properties of the two end products.

Melting points of both jojobamide and homojojobamide are in the range of 75-85 C, depending on the purity of the product. They could be crystallized from petroleum ether. This melting point is relatively high for a mixture of at least 3 products, especially when we compare it with the melting points of the pure components: oleamide 75-76 C (6), eicosenamide, 79-80 C (7), and erucamide 65-66 C (6).

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