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Oxidation and Halogenation of Jojoba Wax

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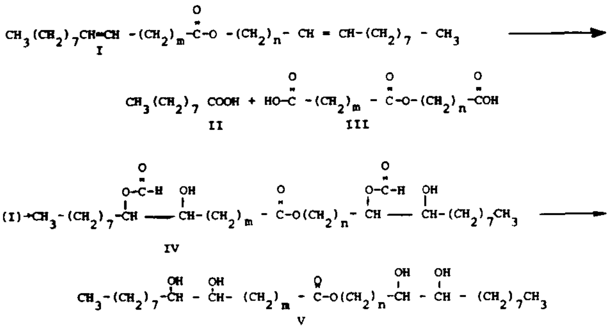
ABSTRACT

The oxidation with hydrogen peroxide and permanganate and the allylic bromination, chlorination and chloro-etherification of the olefinic bonds of the liquid wax extracted from beans of jojoba (*Simmondsia chinensis*) were studied. Hydrolytic splitting of the wax into its carboxylic and alcoholic components competed with most reactions carried out in aqueous systems. The use of a suitable phase-transfer catalyst enabled the oxidation of the double bonds to carboxyls using permanganate in aqueous systems. Reaction of the wax with hydrogen peroxide in formic acid yielded formates, which were then hydrolyzed to vicinal glycols. The diglycols obtained by hydrogen peroxide oxidation were benzoylated. Allylic chlorination of jojoba wax with t-butyl hypochlorite in organic solvents was carried out. Conditions were found for the allylic bromination of the wax, yielding mono-, di-, tetra-, or octabromo derivatives.



INTRODUCTION

The major constituents of jojoba wax, are straight-chain esters of C_{20} and C_{22} monounsaturated alcohols and carboxylic acids (1). In the course of our investigations of the chemical properties of this wax, we set out to develop syntheses for new basic building blocks that could easily be produced from jojoba wax and to determine the reactivity of the wax to various chemical agents. Knowledge of the latter is, of course, a prerequisite for developing uses for the wax and its derivatives either alone or as components of mixtures.

Oxidation of Jojoba Wax with Potassium Permanganate

Jojoba wax (I) was reacted with a cold solution of potassium permanganate in a 2-phase solvent system consisting of water and dichloromethane.

Almost no reaction occurred, even after prolonged stirring. However, the addition of benzyl triethylammonium chloride, as a phase-transfer catalyst, produced a quantitative yield of the cleavage products, pelargonic acid (II) and an α,ω-dicarboxylic acid (III).

The reaction temperature had to be kept below 39 C to avoid further oxidation to shorter carboxylic acids. We also found that the addition of 1-2 equivalents of acetic acid improved the yield by preventing saponification of the ester group. Attempts to oxidize jojoba wax at a basic pH to produce a tetrahydroxy derivative failed. The only reaction taking place was saponification of the ester group.

Oxidation with Hydrogen Peroxide

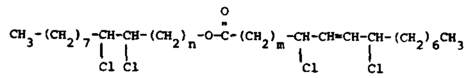
Jojoba wax was treated with hydrogen peroxide in a 2-phase system consisting of benzene and formic acid. Nuclear magnetic resonance (NMR) spectral evidence indicated the formation, in the first stage of the reaction, of a formyl ester (IV), which was then hydrolyzed to the glycol (V). The fresh product had a melting temperature range of 30-40 C. After standing for more than a month, the product turned brittle, probably because of polymerization caused by some peroxides formed during the reaction.

The diglycol of jojoba wax was benzoylated with an excess of benzoyl chloride in pyridine. This benzoylated diglycol polymerizes if exposed to visible light but can be kept for months at room temperature in the dark.

Reaction of Jojoba Wax with *t*-Butyl Hypochlorite

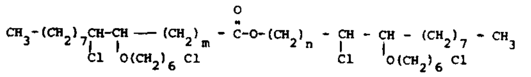
t-Butyl hypochlorite reacts with olefins in alcoholic solutions to give saturated branched β-chloroethers (2). When *t*-butyl hypochlorite reacts with olefins in inert solvents in the presence of radical-forming catalysts, e.g., peroxides, good yields of allyl chlorides are obtained as the sole detectable products. Only in cases where no allylic chlorination is possible, a 1:1 addition takes place, even in the presence of free radicals (3).

Jojoba wax was reacted with 2 equivalents of *t*-butyl hypochlorite in benzene in the presence of benzoyl peroxide, yielding the dichloro derivative (VI). The base peak, m/e = 97, is caused by an allylic fragmentation. According



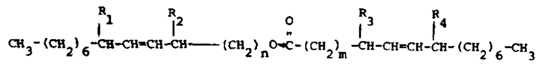
$$CH_3-(CH_2)_7-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-(CH_2)_n-O-\overset{O}{\overset{\|}{C}}-(CH_2)_m-\underset{Cl}{\underset{|}{CH}}-CH=CH-\underset{Cl}{\underset{|}{CH}}-(CH_2)_6CH_3$$

VII



$$CH_3-(CH_2)_7\underset{Cl}{\underset{|}{CH}}-\underset{O(CH_2)_6Cl}{\underset{|}{CH}}-(CH_2)_m-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-\underset{Cl}{\underset{|}{CH}}-\underset{O(CH_2)_6Cl}{\underset{|}{CH}}-(CH_2)_7-CH_3$$

VIII



$$CH_3-(CH_2)_6-\overset{R_1}{\overset{|}{CH}}-CH=CH-\overset{R_2}{\overset{|}{CH}}-(CH_2)_nO-\overset{O}{\overset{\|}{C}}-(CH_2)_m-\overset{R_3}{\overset{|}{CH}}-CH=CH-\overset{R_4}{\overset{|}{CH}}-(CH_2)_6-CH_3$$

VI

to the intensity of the isotopic P + 2 peak, the smallest fragment, containing 2 chlorine atoms, is the following: $[Cl-CH-CH=CH-CH-Cl]$, m/e = 123.

Apparently, the chlorine atoms are on the 2 sides of one double bond. The product, which was obtained by chlorination with 2 equivalents of *t*-butyl hypochlorite without benzoyl peroxide as a catalyst, is also on allylic product, but some addition to the double bond probably occurred at the same time.

When jojoba wax was reacted with 4 equivalents of *t*-butyl hypochlorite in the presence of benzoyl peroxide as catalyst, a compound with allylic chlorination and also with addition to the double bond was obtained (VII).

Concurrent with the halogenation, isomerization to the *trans* form took place; this is especially noteworthy because we found that benzoyl peroxide alone does not cause isomerization. The iodine number and the elemental analysis of chlorine were in agreement with structures VI and VII. The chlorine content of products isolated from reactions carried out in petroleum ether was only 70% of the expected result.

Jojoba wax was reacted with a mixture of *t*-butyl hypochlorite and 6-chlorohexanol in benzene to give the addition compound (VIII).

The reaction was almost quantitative, NMR spectra confirmed the structure and only a slight trace of olefinic bonds could be detected. The position of the chlorine atoms and alkoxy groups may, of course, be inverted, and a random distribution is probably obtained.

Allylic Bromination with N-bromosuccinimide (NBS)

Jojoba wax contains 4 allylic hydrogen atoms at each double bond. Theoretically, 8 bromine atoms may be introduced into 1 molecule of the wax if an excess of N-bromosuccinimide is used. Shani (4) reported the reaction of 2 equivalents of NBS with jojoba oil. We performed the allylic brominations of jojoba wax in carbon tetrachloride in the presence of benzoyl peroxide as catalyst with 1, 2, 4 or 8 equivalents of NBS per equivalent of wax. The products isolated contained 11.2%, 20.7%, 33.7% and 50.1% bromine, respectively, and succinimide was isolated in a 97-99% yield, indicating quantitative bromination. The brominated products exhibited in the infrared (IR) spectrum, a medium-to-strong band at 950-980 cm^{-1}, suggesting that during the bromination *cis-trans* isomerization took place. All the products were unstable liquids, which turned dark on exposure to light after a short period at room temperature.

Attempts to use the above substances as precursors for brominated ethyl esters of jojoba acids failed because reflux of the brominated wax in acidic media seemed to eliminate the bromine.

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