CELLULOSE CHEMISTRY AND TECHNOLOGY

REACTION OF BIXIN WITH ETHYLCELLULOSE IN *N*,*N*-DIMETHYLFORMAMIDE (*N*,*N*-DMF)

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The reaction of ethylcellulose with bixin in *N*,*N*-dimethylformamide and a catalytic amount of anhydrous sodium acetate gave a product characterized by its UV, IR and ^{1}H-NMR spectra data as a reduction product of the bixin-ethylcellulose ether.

Keywords: bixin, *N*,*N*-dimethylformamide, hydride

INTRODUCTION

In our efforts to discover applications for bixin extracted from *Bixa orellana* seeds, other than its predominant use as a colourant,[1,2] the reaction of bixin with ethylcellulose in acetic anhydride, giving a Michael addition product – bixin-ethylcellulose ether – was carried out.[3]

A change in the reaction solvent, *i.e.* the use of *N*,*N*-dimethylformamide instead of acetic anhydride, surprisingly led to the reduction product bixin-ethylcellulose ether. As known, the properties of the solvent affect the mechanism and rate of the reaction.[4]

This reduction is assumed to involve a catalytic “hydride transfer” from *N*,*N*-DMF to the intermediate bixin-ethylcellulose ether, in a quasi-similar manner to the reduction by metallic hydrides.[5] This reduction product of bixin-ethylcellulose is the subject of the present report.

EXPERIMENTAL

Ethylcellulose, purchased from a Chinese Chemical Company, is a commercial product with an average degree of substitution of 2.1, predominantly at the secondary hydroxyl positions.

Bixin was isolated from *Bixa orellana* seeds by the modified method of Jonadiko and Pattenden.[6]

Proton NMR spectra were recorded on a Bruker DRX 400 spectrometer using TMS as an internal standard and $CDCl_3$ as a solvent. Chemical shifts were recorded in ppm as δ-values. The IR spectra were recorded on an Amalect RFX-65 FTIR spectrophotometer, while the UV spectra were measured on a Shimadzu UV-200S double beam spectrophotometer.

The product of the reaction was obtained as follows: 2.0 g (5.0 mmole) of bixin, 0.4 g of ethylcellulose and 0.1 g (1.2 mmole) of sodium acetate were placed in a reaction flask, then 20 mL of *N*,*N*-DMF were added. The mixture thus obtained was flushed with dry N_2, stoppered and stirred on a magnetic stirrer for 3 days at 60 °C, then processed as described in a previous report.[7]

The solid product thus obtained was rinsed several times with ice cold water and, later on, with cold pentane, then rapidly washed with a small amount of cold CH_2Cl_2 and MeOH, to remove the unreacted bixin. Further on, the product was dissolved in CH_2Cl_2, dried with anhydrous $MgSO_4$ and, after filtration, concentrated in vacuum. The bright red solid product (0.85 g) was subjected to UV, IR and ^{1}H-NMR spectral analyses.

RESULTS AND DISCUSSION

Figures 1-3 plot the UV, IR and ^{1}H-NMR spectra of bixin. These spectral data, as well as the melting point, which was found to be between 195 and 197 °C, are in excellent agreement with the existing literature data on bixin.[6,8]

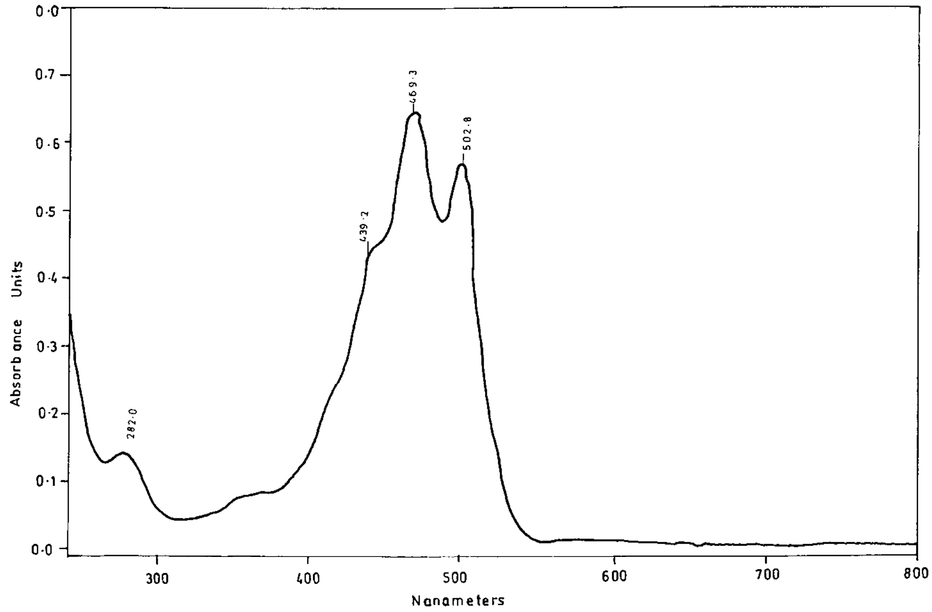


Figure 1: UV spectrum of bixin

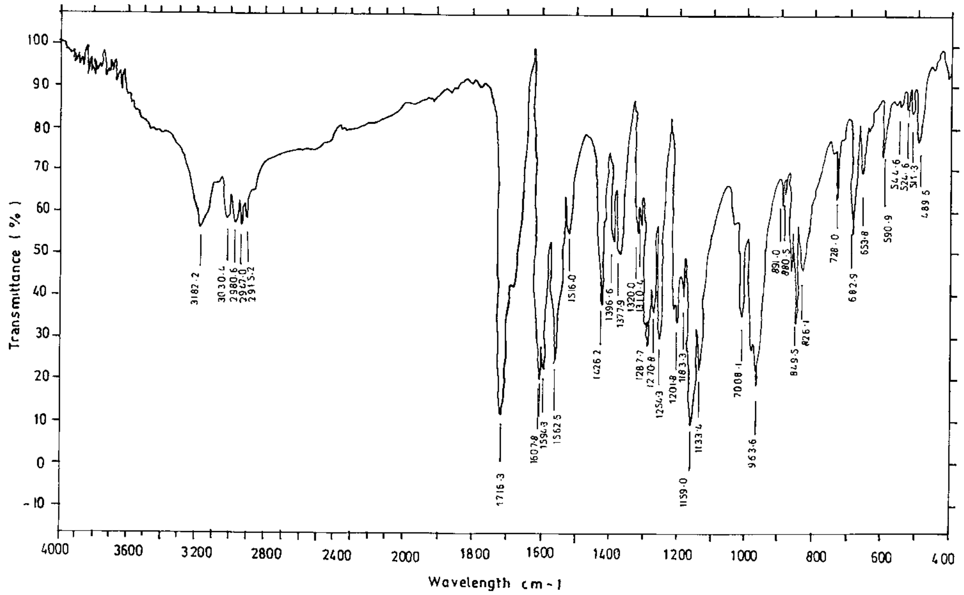


Figure 2: Infrared spectrum of bixin

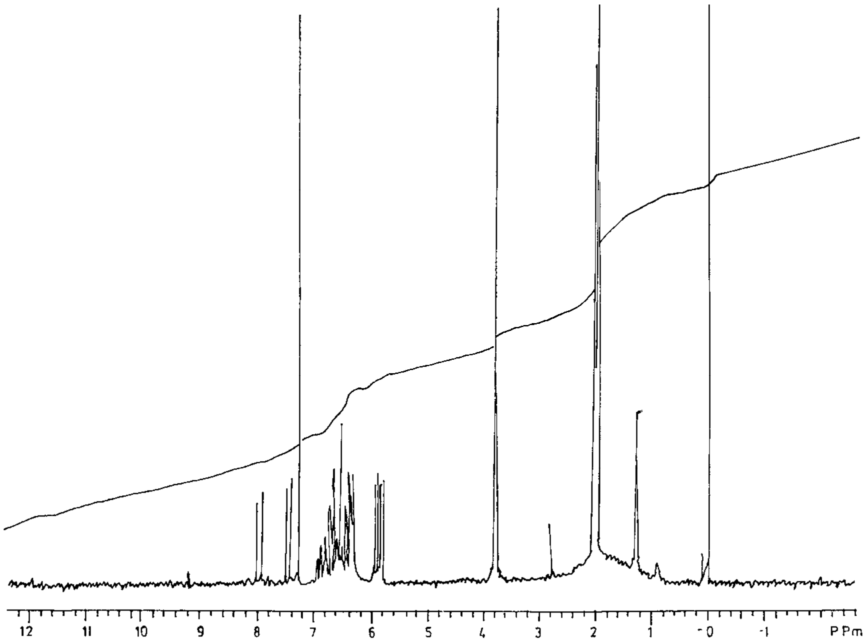


Figure 3: ^{1}H-NMR spectrum of bixin

The UV spectrum of the new ethylcellulose derivative (Fig. 4) shows a hypsochromic shift at λ_{max} between 502.8 and 264.4 nm, which is a clear indication of the extensive loss of unsaturation in the bixin chain, as a consequence of the reduction involving the transfer of the hydride from the solvent, by an unusual mechanism. The fact that the reduction process did occur is confirmed by the absence of the IR signals, which may be attributed to carbon-carbon double bond stretching (Fig. 5).

Similarly, the signals of the methine protons are no longer visible in the proton NMR spectrum of the product (Fig. 6), thereby confirming that the reduction of the double bonds of bixin occurred.

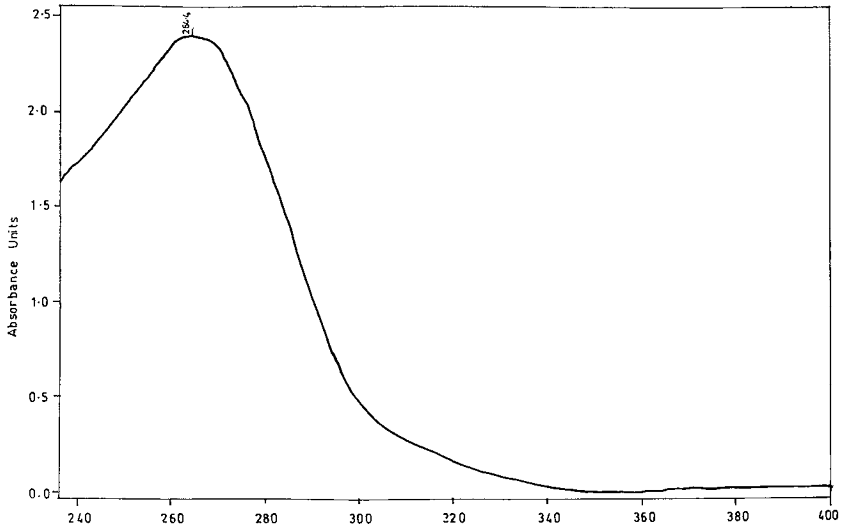


Figure 4: UV spectrum of the product

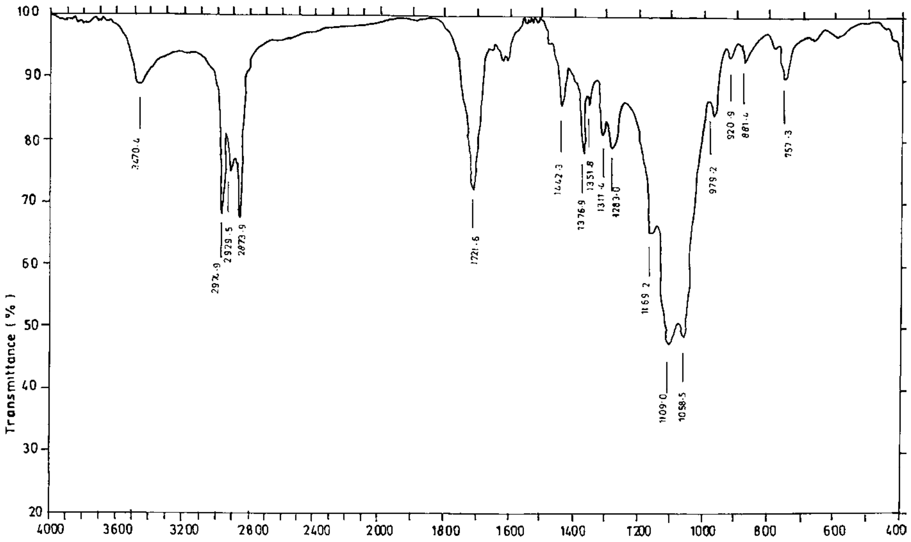


Figure 5: Infrared spectrum of the product

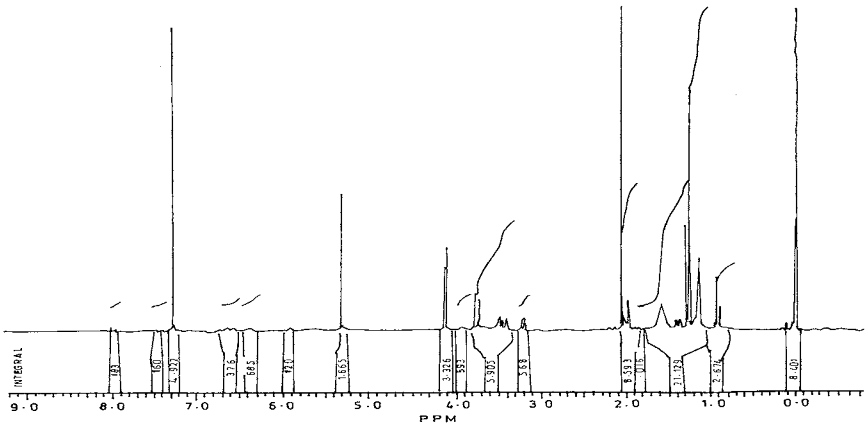
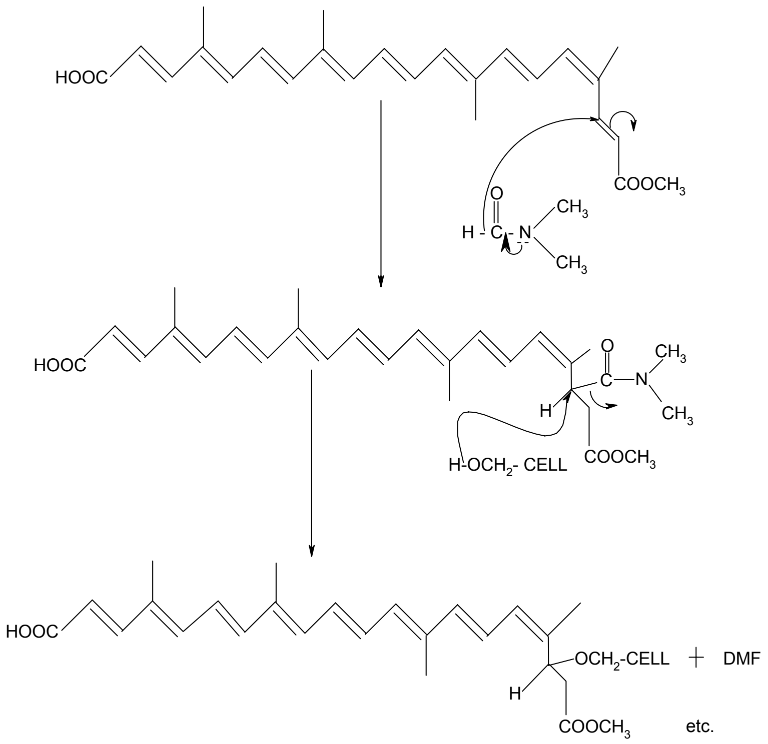


Figure 6: ^{1}H-NMR spectrum of the product

The incorporation of ethylcellulose into the product is confirmed by the important signal present between δ 3.20 and δ 4.20 ppm, induced by the CH_2O groups in ethylcellulose.

One may therefore assert that this unusual reduction occurred first by the catalytic transfer of the "hydride ion" from the *N*,*N*-DMF and that DMF is regenerated by a subsequent attack of a primary hydroxyl group of ethylcellulose, as presented in the reaction scheme below (Scheme 1):



Scheme 1: Proposed mechanism for the formation of the product

The process is repeated to give the new saturated bixin-ethylcellulose derivative. However, the extent to which the reduction has taken place is not yet clearly understood exclusively from the spectra. Further study is necessary to explain how far the regenerated *N*,*N*-DMF performed further reduction of the other double bonds in the bixin chain, to give a structure with a UV-λ_{max} agreeing with the observed value of 264 nm.

CONCLUSIONS

The study evidences that, by DMF mediation, the Michael addition of ethylcellulose to bixin occurred concurrently with the partial reduction of the double bonds of bixin.

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