Isolation and Identification of *trans*-3,5-Dimethoxystilbene from High Quality Tall Oil Fatty Acids by Liquid Chromatography and Mass Spectrometry[1]

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ABSTRACT

trans-3,5-Dimethoxystilbene has been isolated from high quality tall oil fatty acids (unsaponifiables 1.5% maximum, rosin acids 1.5% maximum), using liquid column chromatography and low temperature solvent fractional crystallization. The structure of this compound was determined with the aid of IR, mass and NMR spectrometry. The *trans*-3,5-dimethoxystilbene was found to be responsible for the development of a red color during the epoxidation of the tall oil fatty acids.

INTRODUCTION

Tall oil fatty acids are an important byproduct of the kraft or sulfate pulping process. The current production of tall oil fatty acids in the U.S. is over 370 million pounds per year, which is ca. 40% of the U.S. production of all fatty acids. Even though the demand for tall oil fatty acids continues to increase and more uses for them are constantly being found, their use is hampered by some defects. For example, their usage in the manufacture of epoxy esters for plasticizing agents has been limited because of the development of a red color during the epoxidation step.

The isolation and identification of the component or components which are responsible for the formation of a red color during epoxidation of tall oil fatty acids is of major interest to the tall oil industry (1,2). Cox first reported the presence of 3,5-dimethoxystilbene as a component of the unsaponifiables of wood rosin in 1940 (3). Later, Albrecht and Sheers isolated this compound by batch vacuum refractionation of unsaponifiables extracted from commercial tall oil fraction heads, a fraction boiling at 203-208 C (4 mm), and determined its structure by conventional analysis of its picrate (4). Hetman et al. in a short communication suspected that this compound is responsible for the red color which develops when the tall oil fatty acids are treated with an epoxidizing solution (5).

The present paper reports the isolation of *trans*-3,5-dimethoxystilbene from high quality tall oil fatty acids by a combination of liquid chromatography and low temperature fractional crystallization and the identification of its structure by IR, mass and NMR spectrometry. Data are also furnished to indicate that this compound is responsible for the development of a red color in the presence of epoxidizing agents.

EXPERIMENTAL PROCEDURES

Isolation of Minor Constituents

High quality tall oil fatty acids (7500 g) were passed through five 4.4 x 55 cm columns of silicic acid (Mallinckrodt 2847) simultaneously. The columns were then eluted with hexane. The portion that passed through the columns was combined with the hexane eluate and considered to be the purified tall oil fatty acids. The minor constituents retained on the columns were then eluted with

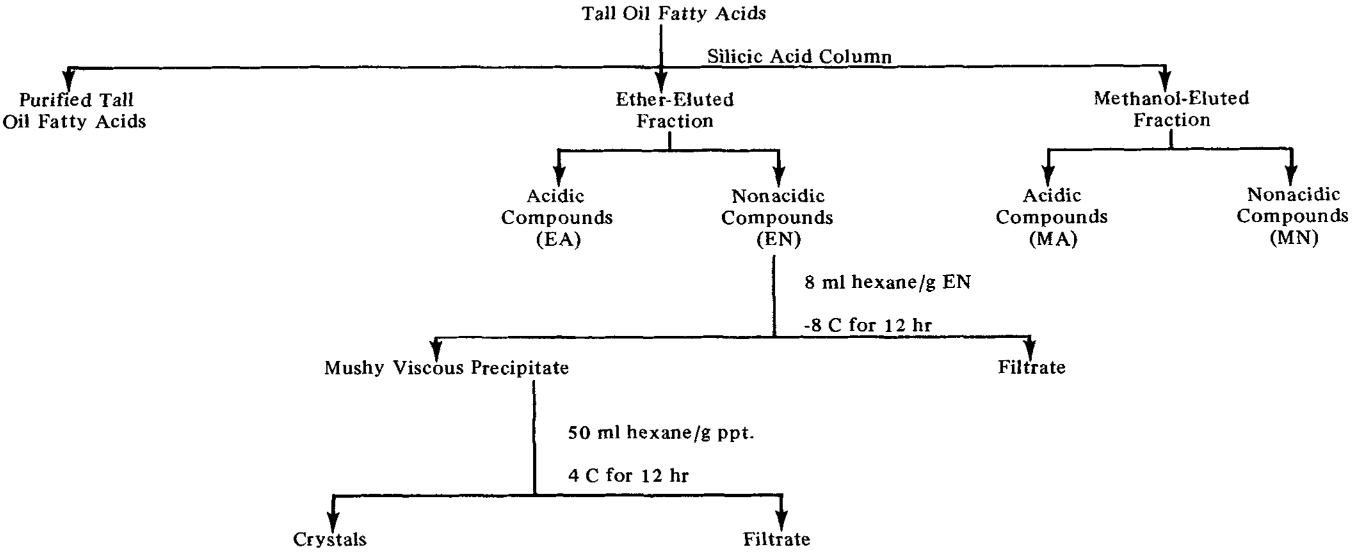

FIG. 1. Isolation of 3,5-dimethoxystilbene from tall oil fatty acids.

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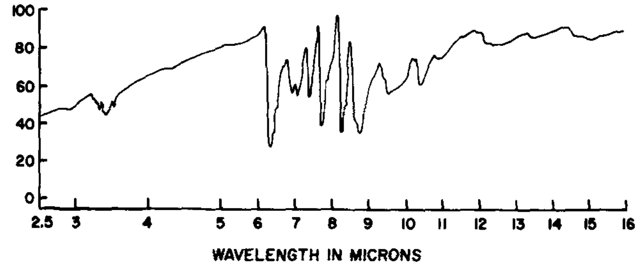


FIG. 2. IR spectrum of the compound identified as *trans*-3,5-dimethoxystilbene.

ethyl ether, followed by methanol.

The ethyl ether eluate was separated into acidic and nonacidic compounds by extracting with 5% aqueous KOH solution. The methanol eluate was separated similarly after the solvent was removed and the residue was dissolved in ethyl ether.

Four groups of minor constituents–namely, the ethyl ether-eluted acidic compounds (EA), the ethyl ether-eluted nonacidic compounds (EN), the methanol-eluted acidic compounds (MA) and the methanol-eluted nonacidic compounds–(MN) were thus obtained (Figure 1).

Isolation of *trans*-3,5-dimethoxystilbene

The ether-eluted nonacidic portion was fractionated by low temperature solvent fractional crystallation in order to isolate the compound(s) which is responsible for the development of the red color upon epoxidation (Fig. 1). In order to accomplish this, 1.0 g of the EN fraction was added to 8 ml hexane and the solution maintained at -8 C for 12 hr. The mushy viscous precipitate thus obtained was filtered and further purified by dissolving in hexane at a rato of 1.0 g/50 ml hexane and storing the solution at 4 C for 12 hr. Slightly yellow crystals were precipitated, which were recrystallized from anhydrous ethanol to yield a white needle-like crystalline solid. The crystals melted sharply at 56.5 C.

Spectrophotometric Methods

The IR spectrum was determined with the use of a Beckman IR -8 spectrophotometer. The sample was made into a 1% KBr pellet.

The mass spectrum was obtained with a Hitachi-Perkin-Elmer RMU-7 single focusing mass spectrometer.

The NMR spectrum was recorded in carbon tetrachloride with tetramethylsilane as the internal reference. A Varian Associates Model T-60 high resolution NMR spectrometer was used.

Epoxidation Method

The epoxidation process was carried out by dissolving 5 ml tall oil fatty acids in 5 ml acetic acid while chilling in ice water. Then 10 ml chilled 40% peracetic acid was added to the above solution. The mixture was well shaken and then allowed to stand in an ice water bath before the color was observed (6).

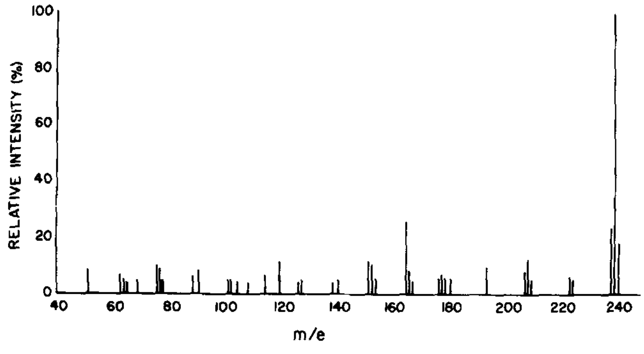


FIG. 3. Mass spectrum of the compound identified as *trans*-3,5-dimethoxystilbene.

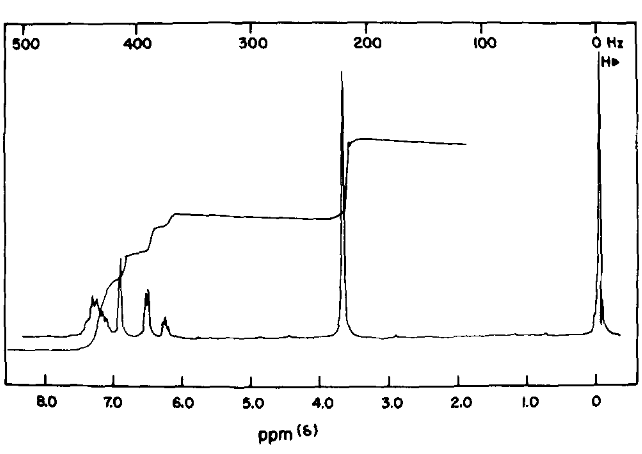


FIG. 4. NMR spectrum of the compound identified as *trans*-3,5-dimethoxystilbene.

RESULTS AND DISCUSSION

Effect of the Minor Constituents upon the Development of Red Color During Epoxidation

The original commercial tall oil fatty acids produced a strong red color when treated with an epoxidizing solution, whereas the purified tall oil fatty acids showed no discoloration under identical conditions.

The effect of four groups of minor constituents (EA, EN, MA, MN) upon the development of discoloration in purified tall oil fatty acids was determined by adding 0.01 g of each group to 5 ml purified tall oil fatty acids (0.2%) and epoxidizing the mixture. The methanol-eluted acidic compounds (MA) caused no discoloration, while the methanol-eluted nonacidic compounds (MN) and the ethyl ether-eluted acidic compounds (EA) caused an insignificant color change. On the other hand, the ethyl ether-eluted nonacidic fraction was found to produce an intense red color after epoxidation. Therefore it was possible that the slight discoloration caused by the MN and EA fractions was due to the presence of a trace amount of the EN fraction.

The addition of the isolated crystalline compound, which was subsequently identified as *trans*-3,5-dimethoxystilbene, to the purified tall oil fatty acids caused a strong red discoloration after epoxidation. This development of red color by the isolated crystalline compound was observed during epoxidation even in the absence of the purified tall oil fatty acids. This seems to indicate that there is no interaction between tall oil fatty acids and the isolated compound during the discoloration upon epoxidation.

To determine whether there was a synergistic effect among the four fractions of minor constituents upon the development of discoloration, the following combinations were added to purifed tall oil fatty acids before epoxidation: EA + EN, MA + EN and MN + EN. No synergistic effect was found in any of these combinations.

It was estimated that the high quality commercial tall oil fatty acids (unsaponifiables 1.5% maximum, rosin acids 1.5% maximum) contained ca. 0.3% of *trans*-3,5-dimethoxystilbene. Since the epoxidation test adopted in this investigation used only 0.2% of the minor constituents, it is evident that the amount of *trans*-3,5-dimethoxystilbene in even the high quality commercial tall oil fatty acids could still cause significant discoloration during epoxidation.

Confirmation of Chemical Structure

The isolated crystalline compound was identified as *trans*-3,5-dimethoxystilbene by a combination of IR, mass and NMR spectrometry. The IR spectrum as shown in

Figure 2 showed a strong band at 10.4 μ which is due to the out-of-plane bending vibration of two hydrogens in opposite directions. This suggests a *trans* double bond in the molecule (3). The strong band at 6.3 μ which is due to the aromatic -C = C- stretching suggests that this compound has an aromatic ring (7).

The mass spectrum of this compound (Fig. 3) has a molecular ion at m/e 240. The presence of ions at m/e 225, 210, 209 and 178 is due to the cleavage of CH_3 CH_3 + CH_3, OCH_3 and 2 OCH_3 from the molecular ion, respectively. This indicates the presence of two OCH_3 groups in the molecule. The peaks at m/e 76, 77, 78 and 91 show the presence of an aromatic ring.

The integration of the NMR spectrum of the isolated crystalline compound showed the presence of five peaks in the ratio of 6:1:2:2:5, from the upper field peak to the lower field peak (Fig. 4). The singlet at δ3.7 represents six protons in the OCH_3 region. Therefore the compound must contain two equivalent methoxy groups.

Since the triplet centered at δ6.2 is due to spin coupling of the proton at the 4 position with protons at the 2 and 6 positions through the double bond of the benzene ring, the two methoxy groups are evidently substituted in the 3 and 5 positions.

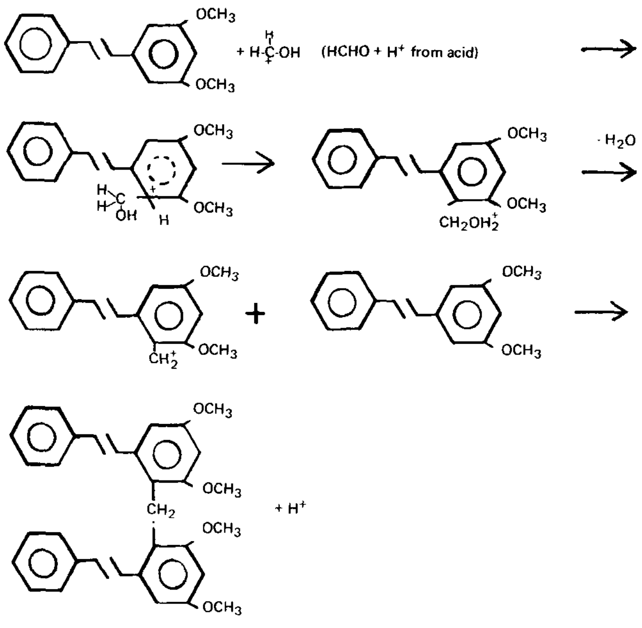
The possibility that the two OCH_3 groups are at the 2, 6 positions are ruled out, even though there is a singlet at δ3.7. This is because the spin spin coupling constant (J) in Figure 4 is ca. 2.0 Hz. It is known that the spin spin coupling constant (J) in aromatic systems between ortho positions is 6.0-9.4 Hz, and that between meta protons is 1.2-3.1 Hz (8).

The doublet peaks at δ6.5 in the NMR spectrum are due to symmetrical hydrogens at the 2 and 6 positions. The crude singlet at δ6.9 is due to two protons of *trans* double bond (9). Multiplets of five protons at δ7.3 are due to the protons in the benzene ring.

Possible Removal of *trans*-3,5-Dimethoxystilbene from Tall Oil Fatty Acids by Heating with Formaldehyde

Two U.S. patents (1,2) claimed that tall oil fatty acids that do not cause the development of red color can be produced by heating with formaldehyde in the presence of an inorganic acid catalyst and distilling the thus treated fatty acids. The patents offered no explanation as to the chemical mechanism of this treatment, The present identification of *trans*-3,5-dimethoxystilbene may offer an explanation.

If 3,5-dimethoxystilbene is present in tall oil fatty acids, it will be dimerized when it is heated with formaldehyde. The dimer would have a higher melting point and would stay in the residue during the distillation step in the manufacture of tall oil fatty acids.



2.2″-Methylenebis(*trans*-3,5-dimethoxystilbene)

ACKNOWLEDGMENTS

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