Trace Components of Tall Oil Fatty Acids: *Trans*-3, 5-Dimethoxystilbene

Abstract

2,2″-Methylenebis(*trans*-3,5-dimethoxystilbene) has been isolated from tall oil fatty acid after reaction with paraformaldehyde in the presence of an acid catalyst.

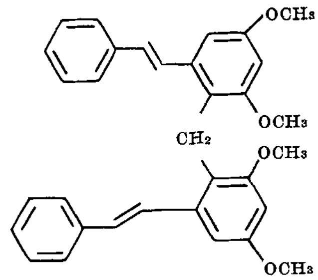
Our continuing interest in trace components in tall oil and tall oil fatty acids was recently stimulated by two patents (1,2) which show heat treatment of tall oil fatty acid with formaldehyde in the presence of an acid catalyst. The resulting fatty acid product, after distillation, no longer gives a red color when treated with an epoxidizing solution. Consequently, lighter colored secondary plasticizers of the epoxy ester type may be prepared from tall oil fatty acids treated in this manner.

We assumed that this red color could be ascribed to *trans*-3,5-dimethoxystilbene, an extractive component of certain pines (3) which we established earlier as a minor component of tall oil by isolation from a tall oil fatty acid heads cuts (4). To demonstrate this, we treated a tall oil fatty acid with formaldehyde and acid clay (Super Filtrol activated clay, Filtrol Corporation) and then carefully distilled (pot temperature 213–216 C, vapor temperature 191–193 C, pressure 1.2 mm) the product. As expected, the starting material which gave a red color prior to treatment, did not after distillation. By following the ultraviolet absorption at about 300 $m\mu$, we demonstrated that the ultraviolet absorption remained in the distillation residue. The present note reports our identification of this absorber as a *trans*-3,5-dimethoxystilbene derivative.

An 1100 g sample of tall oil fatty acid (unsaponifiables 2.7%, rosin acids 4.1%) was treated with 0.5% paraformaldehyde on a steam bath 1½ hr in the presence of 1% Super Filtrol clay and was filtered immediately. Vacuum distillation of the filtrate gave a 1.0% heads cut, a 91.8% main cut and a 4.1% residue (recovery 96.9%). The residue was cooled carefully and a small amount of white crystalline solids deposited slowly. After filtration and trituration of the mushy crystals with petroleum ether, the crude product was recrystallized from benzene to yield white needles with a sharp melting point of 192–193 C.

The ultraviolet spectrum was very similar to that of *trans*-3,5-dimethoxystilbene (5) with an absorption maximum at 304 $m\mu$, a = 86.1 (*trans*-3,5-dimethoxystilbene λ max = 300 $m\mu$, a = 122.8). The carbon and hydrogen analysis (80.2% C, 6.72% H) agreed with the empirical formula $C_{33}H_{32}O_4$: calculated; 80.5% C, 6.55% H. Infrared analysis indicated the presence of *trans* double bond absorption.

The structure shown below, 2,2″-methylenebis(*trans*-3,5-dimethoxystilbene), was deduced from the above and the nuclear magnetic resonance spectrum (NMR) of the compound.



The NMR spectrum consists of two peaks in the OCH_3 region at 3.72 and 3.74σ, a single peak at 4.21σ, two AB patterns in the $6.2–7.6\sigma$ region and an absorption in the aromatic region centered at 7.25σ, which partially overlaps one of the AB patterns.

One of the AB patterns (chemical shifts 6.72 and 7.37σ, coupling constant $J = 16.0\ H_2$) can be assigned to two olefinic hydrogens in a *trans* arrangement. The other AB pattern (chemical shifts 6.35 and 6.55σ, $J = 2.5\ H_2$) would arise from two aromatic protons which are meta to each other.

To account for the required total of 32 protons by integration of the spectrum, it is necessary to assign two protons to the peak at 4.21σ. It then follows that there are two sets of *trans* double bonds, two sets of two *meta* disposed aromatic protons, and two pairs of methoxy groups, where the sets are equivalent by symmetry. This is all nicely accounted for if we assign the 4.21σ peak to the protons in a methylene bridge as shown. The relatively high-field position of these protons is explained by adjacent *ortho* methoxy groups. It is clear that the bridge is attached to the 2 position (rather than the 4 position), because of the nonequivalence of the *meta* aromatic protons.

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REFERENCES

1. Hampton, B. L., (The Glidden Co.), U.S. Patent 3,066,160 (1962).
2. Bried, E. A., (Hercules Powder Co.), U.S. Patent 3,207,743 (1965).
3. Wise, L. E., and E. C. Jahn, "Wood Chemistry," Vol. 1, Reinhold Publishing Corporation, New York 1952, p. 638.
4. Albrecht, H., and E. H. Sheers, J. Am. Chem. Soc. *76*, 603 (1954).
5. Sheers, E. H., Appl. Spectr., *8*, 144 (1954).

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