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Constituents of Wood Rosin: 3,5-Dimethoxystilbene[1]

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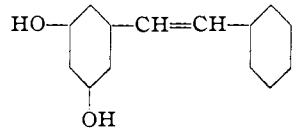
It has been known for many years that both gum and wood rosins contain unsaponifiable material varying in amounts from 4 to 14%. In refined rosins the usual amount found varies from 5 to 7%. According to Knecht and Maurice[2] this consists of pinene, dimers of dipentene and other terpenes, and colophene or rosin oil. A more complete study by Fr. Balas[3] showed the presence of sesquiterpenes and sesquiterpene alcohols having the cadalene skeleton and a paraffin hydrocarbon, *n*-heptacosane.

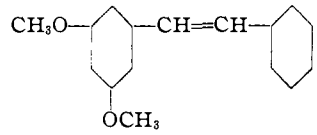
Although both gum and wood rosins contain traces of substances which have methoxyl groups, the isolation of such substances from these rosins has never been reported. In the case of wood rosin, part of the methoxyl analysis is due to methyl ethers of hydroxylated resin acids[4] and part to methoxylated neutral bodies which can be found in the unsaponifiable portion of the rosin.

In the course of an investigation of the constituents of wood rosin in this Laboratory, a neutral crystalline methoxylated substance was isolated. This substance crystallizes from the unsaponifiable portion and sublimes from rosin oil produced by the decarboxylation of wood rosin. By means of oxidation studies, it was shown to be 3,5-dimethoxystilbene (II), a substance not previously found in nature.



Pinosylvin

I



3,5-Dimethoxystilbene

II

Recently, Erdtmann[5] reported the isolation, from the heartwood of the pine tree, of two compounds related to 3,5-dimethoxystilbene. One of these was 3,5-dihydroxystilbene (I), which he called pinosylvin, and the other was the monomethyl ether. He characterized his compounds by methylation to the dimethyl ether melting at 56–57°, the structure of which he proved by oxidation studies. Our 3,5-dimethoxystilbene was identical in melting point with that reported by Erdtmann and could be hydrogenated and subsequently brominated to the same dibromide melting at 142.5–143° (cor.) which he obtained from his dimethylpinosylvin. We further proved the structure by independent oxidation studies with potassium permanganate whereby benzaldehyde, benzoic acid and 3,5-dimethoxybenzoic acid were produced.

The quantity of 3,5-dimethoxystilbene in the unsaponifiable portion of wood rosin is appreciable as shown in Table I where data are given for various rosins.

The amount of 3,5-dimethoxystilbene calculated from the methoxyl content is seen to vary from 12.8 to 37.9%. The amount is least in the refined rosins. The relationship between refractive index and methoxyl content is interesting because it shows that a rough approximation of the dimethoxystilbene content can be made from the refractive index alone. This is possible because of the unusually high refractive index ($n^{30}D$ 1.6450) of 3,5-dimethoxystilbene.

Experimental Part

Separation of Neutral Bodies.—Rosin extracted from pine stumps by benzene had the following properties:

Acid no.	140.3
Saponification no.	167.3
Ester no.	27.0
Unsaponifiable	8.3%
Neutral bodies (ether-soluble)	10.8%
Gasoline-insoluble	21.0%
Petroleum ether-insoluble	26.2%

Five kg. of this rosin was dissolved in 10 liters of alcohol and neutralized at room temperature by the slow addition of 10 liters of water containing 500 g. of sodium hydroxide.

(1) Delivered at the Detroit meeting of the American Chemical Society, Organic Division, September, 1940.

(2) Knecht and Maurice, *J. Soc. Dyers Colourists*, **41**, 356 (1925).

(3) Fr. Balas, *Casopis Ceskoslov. Lekarnictva*, 320–338 (1927); 6–8, 27–31, 47–50 (1928).

(4) The methoxylated resin acids are, in general, gasoline insoluble acids of unknown constitution which occur in crude wood rosin. One of these acids lactonizes readily, forms a crystalline acetate and is similar to but not identical with "sulfite liquor lactone" (Conidendrin) (*Ann.*, **513**, 229 (1934)).

(5) Erdtmann, *Naturwissenschaften*, **27**, 130–131 (1939); *Ann.*, **539** 116–127 (1939); *Svensk Papperstidn.*, **42**, 344–349 (1939).

TABLE I

UNSAPONIFIABLE AND 3,5-DIMETHOXYSTILBENE CONTENT OF ROSINS

Rosin type	Gum	Wood	Wood	Wood	Wood	Vinsol[6]
Rosin color grade	D	K	I	FF	FF	..
% of rosin	9.5	6.5	7.0	7.9	7.3	7.7
Methoxyl content	0.14	3.3	4.0	5.1	5.7	9.8
Refractive index (20°)	1.534	1.545	1.548	1.564	1.565	1.604
Dimethoxystilbene (calcd. %)	0.54	12.8	15.5	19.7	22.1	37.9

This soap solution was exhaustively extracted with petroleum ether and the extract was washed with 2% sodium hydroxide solution in 50% alcohol until no more acidic material was removed. The petroleum ether solution was then concentrated by distillation, the last of the petroleum ether being removed at 60° *in vacuo*. The residue weighed 353 g. It analyzed 5.8% OCH_3.[7]

Saponification of Neutral Bodies.—The neutral bodies extracted above were dissolved in 500 g. of alcohol and saponified by refluxing for 2.5 hours with 18.5 g. of potassium hydroxide. The unsaponifiable matter was removed by adding 500 cc. of water and exhaustively extracting with petroleum ether. The unsaponifiable matter was then freed of acids by washing the extract with 2% sodium hydroxide in 50% alcohol until no more acidic material was removed. The solvent was then removed by distilling, the last of the petroleum ether being removed at 60° *in vacuo*. The weight of unsaponifiable was 200.0 g.

Removal of Dimethoxystilbene.—The unsaponifiable material removed from the neutral bodies of rosin was dissolved in 1000 cc. of petroleum ether and cooled to −60 to −70° with a dry ice–acetone mixture. Crude crystals weighing 17.4 g. separated. They were further purified by dissolving in petroleum ether, filtering through activated carbon and cooling. Beautiful, slightly golden yellow prisms of high refractive index separated.

An additional 14 g. could be frozen out of that portion of the unsaponifiable material boiling in the range 159–218° (14 mm.).

A sample of unsaponifiable material which had stood for several months at room temperature deposited a large crop of large crystals. These were shown by crystallographic comparison to be identical with the crystals removed as described above.

The 3,5-dimethoxystilbene purified by crystallizing from petroleum ether melted at 56.5° (cor.). The purified crystals readily decolorized bromine in carbon tetrachloride and gave a positive test for unsaturation with tetranitromethane in carbon tetrachloride.

Anal. Calcd. for $C_{14}H_{10}(OCH_3)_2$: C, 79.97; H, 6.71; OCH_3, 25.83; mol. wt. 240.29. Found: C, 80.8, 80.5, 80.43, 80.21; H, 6.91, 6.76; OCH_3, 25.5, 25.5; mol. wt. (Rast), 235–244.

Microscopic examination[8] of the crystals of 3,5-dimethoxystilbene showed that they belong to the monoclinic system, holohedral class; the axial angle β = about 55°. Plane of the optic axis is perpendicular to the *b* axis, *Z* makes an angle of about +60° to the *c* axis; dispersion is strong, inclined. Birefringence is high, the refractive index β = about 1.70. The optic angle is nearly 90°. The usual habit is tablets lying on the (001) face, bounded by the (100) and (110) forms. This view shows an optic axis inclined about 20° to the normal, and silhouette angles of approximately 104°, 151°, and 104°. The (011) form is sometimes evident.

The 3,5-dimethoxystilbene was readily supercooled to a viscous oil d^{50}_4 1.092, $n^{50}D$ 1.6358, d^{30}_4 1.109, $n^{30}D$ 1.6450; MR_D calcd. 72.33, found $MR^{50}D$ 78.86, $MR^{30}D$ 78.55.

Chromic Acid Oxidation.—Nine grams of dimethoxystilbene melting at 56.5° was dissolved in 75 cc. of glacial acetic acid. To this was gradually added 8 g. of CrO_3 in 75 cc. of acetic acid at 10°. After fifteen minutes, the mixture was poured slowly into 10 cc. of glacial acetic acid containing 2 g. of sulfuric acid. After one hour, the mixture was diluted with an equal volume of water and extracted with petroleum ether. The extract had the odor of benzaldehyde. The benzaldehyde was removed by steam distillation and was characterized by conversion to dibenzalacetone melting at 112° and the semicarbazone melting at 222°. The residue which may have been dimethoxybenzaldehyde would not yield a semicarbazone.

Bromination.—7.5 grams of dimethoxystilbene melting at 56.5° was dissolved in 50 cc. of ether and to this was gradually added 4.72 g. of bromine in chloroform. The bromine was taken up rapidly with evolution of hydrogen bromide. The solvent was evaporated in a current of air and the residue was recrystallized from methanol and then from ethanol. The chief product melted at 86–86.5°. It was not very soluble in alcohol. *Anal.* Calcd. for $C_{16}H_{15}O_2Br$: OCH_3, 19.4; Br, 25.0. Found: OCH_3, 19.0; Br, 28.2.

4.5 grams of the monobromide melting at 86–86.5° was dissolved in 25 cc. of chloroform, and 1.6 g. of bromine in 25 cc. of chloroform was added slowly. The bromine color disappeared rapidly with evolution of hydrogen bromide. The solvent was removed in a current of air and the residue was crystallized from ethanol. The resulting crystals melted at 85.5–86.5°. A mixture with the monobromide melted at 74–76°. *Anal.* Calcd. for $C_{16}H_{14}O_2Br_2$: OCH_3, 15.6; Br, 40.2. Found: OCH_3, 15.6; Br, 41.1.

Summary

1. The unsaponifiable portion of wood rosin has been shown to contain 3,5-dimethoxystilbene, the dimethyl ether of pinosylvin.

2. Crystallographic and physical properties, and derivatives of 3,5-dimethoxystilbene are reported.

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(6) Gasoline-insoluble resin acids; *cf.* Delaney, *Paint Oil Chem. Rev.*, **97**, No. 12, 32, 34–35 (1935).

(7) E. P. Clark, *J. Assoc. Official Agr. Chem.*, **16**, 136 (1932).

(8) The crystal properties were determined by Mr. Wm. A. O'Brien.