fraction, and cooling in ice gave fine needles of syringic acid, m. p. 209°.[7]

(7) Syringic acid is reported to melt at 205° (uncor. ?).[2]

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Introduction of Double Bonds into Diethyl Stilbestrol

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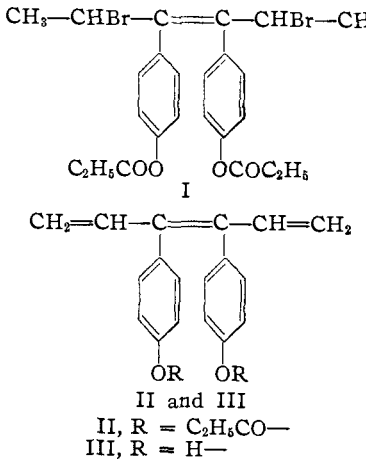
In the course of some work in this Laboratory on synthesizing substances with estrogenic activity, a 3,4 conjugated triene was prepared.

Diethylstilbestrol dipropionate was treated with 2 moles of N-bromosuccinimide to yield 3,4-bis-(*p*-propionoxyphenyl)-2,5-dibromohexene-3 (I). Two moles of hydrogen bromide were then eliminated by treatment with diethylaniline and the resulting 3,4-bis-(*p*-propionoxyphenyl)-hexatriene-1,3,5 (II) saponified to yield the free phenol (III).

The structural formulas of the new compounds are



Absorption spectra of the conjugated triene dipropionate and the free phenol showed two peaks for each substance. The ester showed peaks at 273 and 280 mμ with a rather high molecular extinction coefficient of 22,860 at 280 mμ. The free phenol showed peaks at 223 and 257 mμ with a molecular extinction coefficient of 20,570 at 257 mμ.

Experimental

3,4-bis-(*p*-Propionoxyphenyl)-2,5-dibromo-hexene-3.—Thirty grams of diethylstilbestrol dipropionate dissolved in 300 ml. of carbon tetrachloride and 28.2 g. of N-bromo-succinimide were refluxed for thirty minutes in an atmosphere of nitrogen. The hot mixture was filtered and the crystals of succinimide washed with 15 ml. of carbon tetrachloride. The dried succinimide weighed 15.4 g. (theoretical recovery, 15.7 g.). The filtrate was washed with water to remove the last traces of succinimide, dried over sodium sulfate, filtered, concentrated to a volume of 85 ml. and cooled overnight. The precipitated white crystals were washed with carbon tetrachloride and dried in a vacuum desiccator at room temperature; yield, 27.3 g., m. p. 149°, green melt with decomposition. One recrystallization from carbon tetrachloride yielded small white crystals, m. p. 149.5°.

Anal. Calcd. for $C_{24}H_{26}O_4Br_2$: C, 53.54; H, 4.97; Br, 29.71. Found: C, 53.48; H, 5.10; Br, 30.32.

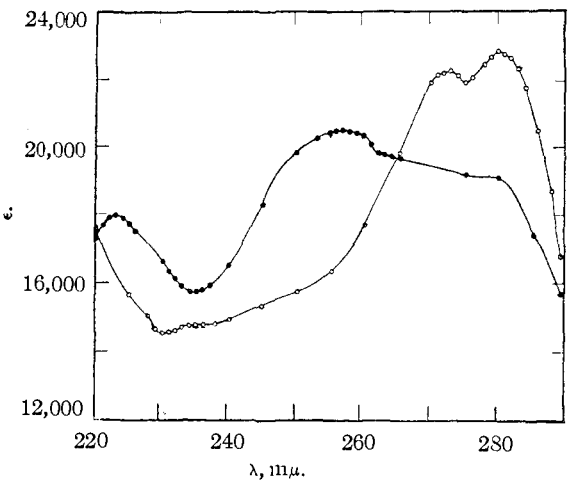


Fig. 1.—Ultraviolet absorption spectra of 3,4-bis-(*p*-propionoxyphenyl)-hexatriene-1,3,5, -O-; 3,4-bis-(*p*-hydroxyphenyl)-hexatriene-1,3,5, -●-.

3,4-bis-(*p*-Propionoxyphenyl)-hexatriene-1,3,5.—Twenty-one and eight-tenths grams of the above dibromo compound was heated at 150–160° for ten minutes with 220 ml. of diethylaniline. The solution darkened considerably and then was cooled to room temperature, after which it was acidified with concentrated hydrochloric acid and extracted three times with 250-ml. portions of ether. The combined ether extracts were washed with water until neutral, dried over sodium sulfate, and concentrated to a volume of 75 ml. This was then cooled to −50°, filtered and washed with a small amount of cold ether. The seven and one-tenth grams of crude crystals (m. p. 128–132°) after recrystallization from 150 ml. of petroleum ether yielded 5.4 g. of long, white needles, m. p. 134–136°.

Anal. Calcd. for $C_{24}H_{24}O_4$: C, 76.58; H, 6.43. Found: C, 76.70; H, 6.59.

When treated with bromide-bromate reagent, the triene dipropionate took up 3.84 atoms of bromine.

3,4-bis-(*p*-Hydroxyphenyl)-hexatriene-1,3,5.—Two grams of the dipropionate was refluxed for twenty minutes with 65 ml. of 10% potassium hydroxide in methanol. After this time, three volumes of water was added, and the solution made slightly acid with concentrated hydrochloric acid. At this point, the free phenol which had precipitated out, was filtered off and crystallized from ether–petroleum ether yielding 1.3 g. of slightly yellowish crystals, m. p. 196–198°. After recrystallization from aqueous isopropanol, 0.8 g. of white needles was obtained, m. p. 202–203°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.82; H, 6.11. Found: C, 81.70; H, 6.14.

Absorption Spectra.—The spectra were determined with a Beckman quartz spectrophotometer, density readings being made at 5 mμ intervals, except when in the region of maxima or minima when the readings were made at 1 mμ intervals.

The solvent used for both curves was 99% isopropanol (Carbide & Carbon). This solvent was not purified in any way since readings could be obtained when the wave length was as low as 217 mμ.

The concentration of the conjugated dipropionate was 7 mg. per liter and that of the free phenol was 7.6 mg. per liter, and the thickness of the silica absorption cells was 1.000 ± 0.002 cm.

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