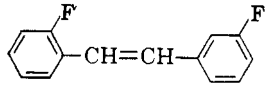
TABLE I

Carbinol	B.p., °C./mm.	n_D	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ethyl-*p*-fluorophenyl	116/17	1.5004/28°	$C_9H_{11}FO$	70.1	70.0	7.1	7.0
Propyl-*o*-fluorophenyl	124/17	1.4958/28°	$C_{10}H_{13}FO$	71.4	71.1	7.7	7.7
Isopropyl-*p*-fluorophenyl	115/17	1.4963/28°	$C_{10}H_{13}FO$	71.4	71.1	7.7	7.8
Butyl-*p*-fluorophenyl	132/17	1.4901/21.5°	$C_{11}H_{15}FO$	72.5	72.3	8.2	8.4
Isobutyl-*p*-fluorophenyl	128/17	1.4938/28°	$C_{11}H_{15}FO$	72.5	72.2	8.2	8.5
Amyl-*p*-fluorophenyl	148/17	1.4953/19°	$C_{12}H_{17}FO$	73.5	73.4	8.7	8.7
Isoamyl-*p*-fluorophenyl	143/17	1.4937/24°	$C_{12}H_{17}FO$	73.5	73.3	8.7	8.6
Isohexyl-*p*-fluorophenyl	149/17	1.4862/26.5°	$C_{13}H_{19}FO$	74.3	74.0	9.0	9.0
β-Phenethyl-*p*-fluorophenyl	177/15	1.5732/24°	$C_{15}H_{15}FO$	78.3	78.5	6.5	6.8
γ-Phenylpropyl-*p*-fluorophenyl	185/15	1.5637/25°	$C_{16}H_{17}FO$	78.7	78.6	7.0	7.3
Ethyl-*m*-fluorophenyl	115/17	1.5039/25°	$C_9H_{11}FO$	70.1	70.0	7.1	7.0
Butyl-*m*-fluorophenyl	131/17	1.4975/25°	$C_{11}H_{15}FO$	76.5	76.2	8.2	8.3
Isohexyl-*m*-fluorophenyl	149/17	1.4913/25°	$C_{13}H_{19}FO$	74.3	74.0	9.0	9.2
Octyl-*m*-fluorophenyl	176/17	1.4830/25°	$C_{15}H_{23}FO$	75.6	75.5	9.6	9.5
Dodecyl-*m*-fluorophenyl	214/17	1.4753/24°	$C_{19}H_{31}FO$	77.6	77.3	10.5	10.8
γ-Phenylpropyl-*m*-fluorophenyl	188/17	1.5649/25°	$C_{16}H_{17}FO$	78.7	78.9	7.0	7.3
Methyl-*o*-fluorophenyl	105/17	1.5087/25°	C_8H_9FO	68.6	68.5	6.4	6.6
Propyl-*o*-fluorophenyl	118/16	1.5013/25°	$C_{10}H_{13}FO$	71.4	71.2	7.7	7.9
Amyl-*o*-fluorophenyl	144/16	...	$C_{12}H_{17}FO$	73.5	73.4	8.7	8.7
β-Phenethyl-*o*-fluorophenyl	177/15	1.5730/25°	$C_{15}H_{15}FO$	78.3	78.5	6.5	6.7

fluorophenylcarbinols, prepared from arylalkylmagnesium chlorides, were also included in our investigation. The carbinols readily underwent dehydration by means of formic acid to give the corresponding ethylenes, including the hitherto unknown 2,3′-difluorostilbene (I) and 3,4′-difluorostilbene (II).



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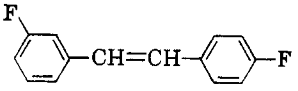

II

In biological tests in rats, the lower terms of the series of carbinols reported herein displayed pronounced choleretic activity.

Experimental

Preparation of Intermediates.—*o*-, *m*-, and *p*-fluorobenzaldehyde were prepared by the Sommelet reaction from the corresponding fluorobenzyl bromides, themselves obtained from *o*-, *m*-, and *p*-fluorotoluene by side-chain bromination with *N*-bromosuccinimide in the presence of benzoyl peroxide.

Grignard Reactions.—An ethereal solution of a Grignard reagent prepared from the appropriate alkyl iodide or bromide (1.15 moles) was treated portionwise at 0° with the aldehyde (1 mole, dissolved in anhydrous ether). The mixture was refluxed for a few minutes on the water bath, and after cooling, treated with an ice-cold aqueous solution of ammonium chloride. The organic layer was then collected, washed with water, and dried over sodium sulfate, the ether was distilled, and the residue vacuum-fractionated twice. The carbinols thus obtained in 80–90% yield as colorless liquids, are listed in the table.

Dehydration of the Carbinols.—A solution of one part of the carbinol in 5 parts of anhydrous formic acid was heated for 1 hr. on the water bath. The reaction product was poured into water, taken up in benzene, and dried over sodium sulfate, the solvent was removed, and the residue vacuum-fractionated.

1-Fluorophenyl-1-propene, obtained from ethyl-*p*-fluorophenylcarbinol, was a colorless fluid liquid, b.p. 99°/17 mm., n^{14}_D 1.5690.

Anal. Calcd. for C_9H_9F: C, 79.4; H, 6.6. Found: C, 79.6; H, 6.6.

2,3′-Difluorostilbene (I). ***o*-Fluorobenzyl-*m*-fluorophenylcarbinol**, prepared from *o*-fluorobenzylmagnesium chloride and *m*-fluorobenzaldehyde, was a pale yellow oil, b.p. 164°/15 mm.; this underwent dehydration to the **stilbene** (I), which crystallized from pentane in colorless needles, m.p. 43°.

Anal. Calcd. for $C_{14}H_{10}F_2$: C, 77.8; H, 4.6. Found: C, 77.7; H, 4.7.

3,4′-Difluorostilbene (II). ***p*-Fluorobenzyl-*m*-fluorophenylcarbinol**, prepared as above from *p*-fluorobenzylmagnesium chloride, gave on dehydration the *stilbene* (II) which crystallized from hexane in colorless prisms, m.p. 99°.

Anal. Calcd. for $C_{14}H_{10}F_2$: C, 77.8; H, 4.6. Found: C, 77.5; H, 4.6.

Insect Sex Attractants. III. The Optical Resolution of *dl*-10-Acetoxy-*cis*-7-hexadecen-1-ol

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The extremely potent sex attractant secreted by the female gypsy moth (*Porthetria dispar*) to lure the male has been identified previously as dextrorotatory 10-acetoxy-*cis*-7-hexadecen-1-ol (I), and the equally attractive optically inactive (*dl*-) form has been synthesized.[1] The *dl*-form has now been successfully resolved by treating its acid succinate with L-brucine, separating the brucine salts by fractional crystallization from acetone, decomposing the salts, and saponifying the acid succinates with ethanolic alkali. The resulting *d*- and *l*-forms of I were identical in all respects save optical activity with one another, with the *dl*-form, and with the

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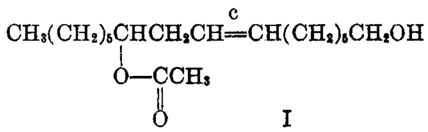
[1] M. Jacobson, M. Beroza, and W. A. Jones, *Science*, **132**, 1011 (1960); *J. Am. Chem. Soc.*, **83**, 4819 (1961).



$CH_3(CH_2)_5CH(OCOCH_3)CH_2CH\overset{c}{=}CH(CH_2)_5CH_2OH$

I

natural attractant, and all forms were equally attractive to male gypsy moths when tested in the field at 10^{-7} microgram/trap.[2]

Experimental

Preparation of the Acid Succinate of *dl*-I.—A mixture of 500 mg. of *dl*-I, 0.3 g. of recrystallized succinic anhydride, and 0.5 ml. of dry pyridine was heated at 100° in a sealed tube for 20 hr., cooled, poured into excess 5% hydrochloric acid, and extracted with several small portions of ether. The combined ethereal extract was washed free of mineral acid with water, extracted with 5% sodium carbonate, and the alkaline extract was acidified with 20% hydrochloric acid and extracted with ether. The ethereal extract was washed free of mineral acid with water, dried over sodium sulfate, and freed of solvent, giving 530 mg. of orange, viscous liquid that resisted repeated attempts at crystallization.

Preparation of the Brucine Salts.—A solution of the acid succinate in 4.5 ml. of acetone was heated to boiling on the steam bath, treated with 1 g. of L-brucine, heated an additional 30 sec., filtered, and cooled in an ice bath with scratching. The white solid that rapidly separated was recrystallized from acetone to give 273 mg. of insoluble brucine salt A, m.p. above 220°, $[\alpha]^{27}\mathrm{D}$ −4.7° (*c* 2.0, chloroform).

The combined acetone filtrate and mother liquors were evaporated to dryness and the residue was taken up in ethyl acetate, washed with water, and dried over sodium sulfate. Removal of the solvent and crystallization of the white residue from 0.5 ml. of acetone at −50° gave 245 mg. of brucine salt B, $[\alpha]^{27}\mathrm{D}$ −5.3° (*c* 2.0, chloroform).

Decomposition of the Brucine Salts.—Brucine salt A (270 mg.) was stirred at room temperature with 15 ml. of 20% hydrochloric acid, and the mixture was allowed to stand for 5 hr. and then extracted with ether. The ether extract was washed free of mineral acid with water, dried over sodium sulfate, and freed of solvent to give 246 mg. of the acid succinate of *d*-I as a pale yellow, viscous oil, $[\alpha]^{27}\mathrm{D}$ +22.4° (*c* 2.0, chloroform), that failed to crystallize.

Decomposition of brucine salt B (240 mg.) in the same manner gave 219 mg. of the acid succinate of *l*-I as a pale yellow, viscous oil, $[\alpha]^{27}\mathrm{D}$ −17.6° (*c* 2.0, chloroform).

Saponification of the Acid Succinates.—A solution containing 246 mg. of the acid succinate of *d*-I, 10 ml. of 10% sodium hydroxide, and 1 ml. of ethyl alcohol was heated on the steam bath for 2 hr., cooled, and extracted with ether, and the extract was washed with water, dried (sodium sulfate), and freed of solvent to give a yellow oil. This oil was dissolved in petroleum ether (b.p. 40–60°) and the solution filtered through a column of 10 g. of cellulose acetate and evaporated to dryness, giving 212 mg. of (+)-10-acetoxy-*cis*-7-hexadecen-1-ol as a colorless liquid, $[\alpha]^{27}\mathrm{D}$ +7.8° (*c* 2.0, chloroform), identical with the natural gypsy moth attractant.[1]

In a similar manner, the saponification of 219 mg. of the acid succinate of *l*-I gave 179 mg. of (−)-10-acetoxy-*cis*-7-hexadecen-1-ol as a colorless liquid, $[\alpha]^{27}\mathrm{D}$ −7.1° (*c* 2.0, chloroform), that solidified in the cold but melted again at room temperature. The infrared spectrum[3] was identical with those of *d*- and *dl*-I.

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[2] These tests were carried out as described by J. M. Corliss, *Yearbook Agr.* (U.S. Dept. Agr.), 694 (1952). The assistance of E. C. Paszek, U.S. Department of Agriculture, Nashua, N. H., in carrying out these tests is gratefully acknowledged.

[3] Determined with a Perkin-Elmer Model 21 spectrophotometer, by means of sodium chloride optics and a 1% solution of the sample in carbon disulfide. Mention of trade names or proprietary products does not necessarily constitute endorsement by the Department of Agriculture.

The Bromination of Ethyl 4-Phenylphenyl Carbonate

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A number of esters of 4-phenylphenol have been brominated, and the results have been reported previously.[1] The chlorination[2] of 4-phenylphenyl acetate resulted in the formation of 4-(4-chlorophenyl)phenyl acetate, although bromination had given a product with the halogen atom at a position in the molecule *ortho* to the acyloxy group.[3] In an attempt to determine the behavior of another ester of 4-phenylphenol in which the acyloxy group is rather small and should have little steric effect at *ortho* positions, the bromination of ethyl 4-phenylphenyl carbonate[4] has been studied.

The results, which are shown in the Experimental, did not indicate that any bromination of the ester occurred *ortho* to the acyloxy group. Rather, substitution occurred in the ester at the most remote position in the biphenyl group, as had been observed in most of the previous investigations; there was evidence that some *ortho* substitution had occurred in free phenols, which were isolated from reaction mixtures. Compounds isolated from reaction mixtures were identified by mixed melting point procedures.

The bromination of ethyl 4-phenylphenyl carbonate proceeds more smoothly in carbon tetrachloride than in glacial acetic acid solution. An improved method for the preparation of 2,6-dibromo-4-(4-bromophenyl)phenol has been developed. Several new esters of bromine substituted 4-phenylphenols are reported.

Experimental

Bromine Substituted 4-Phenylphenols.—These compounds were prepared by methods that have been reported previously, except that 2,6-dibromo-4-(4-bromophenyl)-phenol[5] was prepared by a modification of a procedure[1] that had been used for the preparation of 2-bromo-4-(4-bromophenyl)phenol. 4-Phenylphenol (15 g., 0.088 mole) was suspended in 120 ml. of carbon tetrachloride, a trace of iron powder was added, and while the mixture was stirred and

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[1] S. E. Hazlet and L. C. Hensley, *J. Am. Chem. Soc.*, **69**, 708 (1947) and earlier papers.

[2] C. M. S. Savoy and J. L. Abernethy, *ibid.*, **64**, 2219 (1942).

[3] S. E. Hazlet and H. A. Kornberg, *ibid.*, **61**, 3037 (1939).

[4] E. Baumgarten, H. G. Walker, and C. R. Hauser, *ibid.*, **66**, 303 (1944).

[5] F. Bell and P. H. Robinson, *J. Chem. Soc.*, 1131 (1927).