tested for uterotrophic[4] and antiuterotrophic[4] activities in the mouse. It was dissolved in olive oil and injected subcutaneously. It displayed no significant activities in 3 daily doses of as much as 300 μg. *In vitro* the thiophenol II showed no competitive binding affinity[4] for estrogen "receptor" sites of the mouse uterus in concentrations 10^3 times the effective concentrations of I.

Experimental Section

meso-**3,4-Hexanebis(phenyl-4-disulfonyl chloride).**—To a solution of 3 g (0.013 mole) of *meso*-3,4-diphenylhexane[5] in 20 ml of dry CCl_4 in a dry atmosphere was added 6 g (0.05 mole) of $ClSO_3H$ and the mixture was stirred for 12 hr at room temperature. The suspension was filtered. The product (8.5 g) was crystallized from $CHCl_3$ after which it melted at 220–226°. *Anal.* ($C_{18}H_{20}Cl_2S_2O_4$), C, H, S.[6]

meso-**3,4-Hexanebis(phenyl-4-thiol) (II).**—The crude disulfonyl chloride was reduced according to a literature procedure.[7] $SnCl_2 \cdot 2H_2O$ (10 g) and 50 ml of HAc was saturated with anhydrous HCl. The solution was maintained at 80°, 6.5 g (0.015 mole) of the sulfonyl chloride was added and the solution was stirred for 1 hr. The solution was cooled, poured into 30 ml of concentrated HCl, and filtered. The filtrate was extracted (Et_2O), dried, and crystallized several times from C_6H_6. The product was sublimed at 170° (0.01 mm); yield 1 g (25%), mp 147–150°.[3] *Anal.* ($C_{18}H_{22}S_2$) C, H, S.[8] Absorption bands (or peaks) of spectra (nmr, ir) were as expected.

Acknowledgments.—Nmr spectra were kindly recorded by Dr. S. O. Almquist at the Department of Chemistry, College of Agriculture, Uppsala. This work was supported by the Swedish Cancer Society.

(4) L. Terenius, *Mol. Pharmacol.*, **4**, 301 (1968).
(5) S. Wawzonek, *J. Amer. Chem. Soc.*, **68**, 1157 (1946).
(6) C: calcd, 49.7; found, 49.1; S: calcd, 14.8; found, 15.6.
(7) C. S. Marvell and P. D. Caesar, *J. Amer. Chem. Soc.*, **73**, 1097 (1951).
(8) The analyses were within ±0.4% of theoretical values. Melting points are uncorrected.

Compounds Related to Insect Juvenile Hormone. V. Derivatives of Citronellol and Citronellylamine

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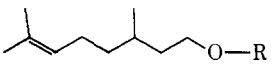
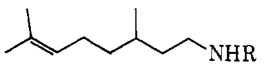
A number of investigators have reported that certain compounds having insect juvenile hormone activity are also inhibitors of embryonic development in some species of insects.[1] Also, the "dihydrochloride" of methyl farnesate has been found to be a very effective sterilant for female *Pyrrhocoris apterus* (L.).[2] In addition, Masner and coworkers described the phenomenon of sexually spread insect sterility that occurred when they used compounds with known juvenile hormone activity.[3]

Among the compounds best known for their chemosterilant activity are tepa [tris(1-aziridinyl)phosphine oxide][4] and hempa (hexamethylphosphoric triamide).[4,5] We therefore prepared a number of derivatives of citronellol (3,7-dimethyl-6-octenol) and citronellylamine (3,7-dimethyl-6-octenylamine), several of which bear a structural resemblance to these sterilants, for testing as potential sterilants and juvenilizers. The test compounds are listed in Table I.

Table I

R	Bp, °C(mm)	Yield, %	Formula
A. Compounds Derived from Citronellol (3,7-Dimethylethyl-6-octen-1-ol)			
			
$-P(O)[N(CH_3)_2]_2$	128–133(0.15)	63	$C_{14}H_{31}N_2O_2P$
$-P(O)(N\triangleleft)_2$	142–150(0.10)	53	$C_{14}H_{27}N_2O_2P$
$-C(O)N(CH_3)_2$	83–89(0.05)	90	$C_{13}H_{25}NO_2$
$-CN\triangleleft$ (O)	84–93(0.05)	86	$C_{13}H_{23}NO_2$
B. Compounds Derived from Citronellylamine (3,7-Dimethyl-6-octenylamine)			
			
$-CO_2C_2H_5$	102–103(0.10)	87	$C_{13}H_{25}NO_2$
$CONH(CH_2)_6NHC(O)$	138–139[a]	97	$C_{28}H_{54}N_4O_2$
$-P(O)[N(CH_3)_2]_2$	165–180(0.10)[b]	27[b]	$C_{14}H_{32}N_3OP$
$-P(O)(N\triangleleft)_2$	165–180(0.10)[b]	24[b]	$C_{14}H_{28}N_3OP$[c]
C. Miscellaneous			
$R'CO_2C_2H_5$[d]	107–111(0.12)	72	$C_{13}H_{23}NO_2$
$R''CO_2C_2H_5$[e]	123–130°(0.03)	84[f]	$C_{13}H_{25}NO_3$

[a] Melting point following recrystn from EtOH. [b] Decomposes on distn. [c] Combustion analyses were poor, but the nmr spectrum (see Experimental Section) was entirely consistent. [d] Commercial citral was converted into its oxime and reduced with LAH to a mixture of cis and trans amines. R′ therefore is (3,7-dimethyl-2,6-octadienyl)amino. [e] R″ is (6,7-epoxy-3,7-dimethyloctyl)amino. [f] Yield of the epoxidation step.

Only *P,P*-bis(1-aziridinyl)-*N*-(3,7-dimethyl-6-octenyl)phosphinic amide showed chemosterilant activity against house flies, *Musca domestica* L. The carbamates and their epoxides were the only compounds to show juvenile hormone activity against *Tenebrio molitor* L.[6,7]

Experimental Section

The chem anal. were performed by Galbraith Associates, Inc., Knoxville, Tenn. Nmr spectra were obtained with a Varian Model T-60 instrument, and ir spectra were recorded as films or mulls with a Perkin-Elmer 137 ir spectrophotometer. Where analyses are indicated only by symbols of the elements, analytical results obtained for those elements were within ±0.4% of the theoretical values (see Table I).

Citronellol Derivatives.—Citronellol was converted into its chloroformate by treatment with 1 equiv each of $COCl_2$ and Et_3N. An ethereal soln of $COCl_2$ was added dropwise to a well-stirred soln of the alcohol and amine in Et_2O while the mixture was held at 20–30°. The mixture was allowed to stand at room temp for 1.5 hr and filtered by suction (Et_2O rinse). The filtrate

(1) K. Sláma, and C. M. Williams, *Nature (London)*, **210**, 329 (1966); L. M. Riddiford, and C. M. Williams, *Proc. Nat. Acad. Sci. U. S.* **57**, 595 (1967).
(2) P. Masner, K. Sláma, and V. Landa, *J. Embryol. Exp. Morphol.*, **20**, 25 (1968).
(3) P. Masner, K. Sláma, and V. Landa, *Nature (London)*, **219**, 395(1968).
(4) G. C. LaBrecque, *J. Econ. Entomol.*, **54**, 684 (1961).
(5) S. C. Chang, P. H. Terry, and A. B. Borkovec, *Science*, **144**, 57 (1964).
(6) W. S. Bowers, and M. J. Thompson, *ibid.*, **142**, 1469 (1963).
(7) Mention of a pesticide or a proprietary product in this paper does not constitute a recommendation or endorsement of this product by the U. S. Department of Agriculture.

was washed with H_2O, dried ($MgSO_4$), and concd. The yield of crude product was 89% (C=O, 1780 cm^{-1}). The chloroformate was converted into the desired carbamate by adding 1 equiv each of an amine (ethylenimine or Me_2NH) and Et_3N. The conditions and work-up procedure paralleled those just described.

Citronellol was converted into the P derivatives by treatment with 1 equiv each of the required acid halide and Et_3N.

Citronellylamine Derivatives.—The amine was prepared by LAH reduction of the oxime.[8] However, yields were variable and depended largely on the freshness of the reducing agent. Citronellylamine reacted with hexamethylene diisocyanate in Et_2O exothermically to produce the diurea as a ppt. The amine was converted into its other listed derivatives by reaction with the acid halide and Et_3N as described for citronellol.

Epoxidation of the ethyl (3,7-dimethyl-6-octenyl)carbamate was carried out with 1 equiv of *m*-chloroperbenzoic acid in CH_2Cl_2. The mixture was held at 5–10° during addn of the olefins and was allowed to stand at room temp overnight. After extraction with Na_2CO_3, the organic soln was dried (Na_2SO_4), concd, and dist by using a short-path distn apparatus.

The nmr spectrum of *P,P*-bis(1-aziridinyl)-*N*-(3,7-dimethyl-6-octenyl)phosphinic amide showed the following absorptions: 0.88 d (CH_3CH), 1.57 and 1.65 (cis and trans allylic Me, respectively), 1.93 d (—N  , J_{PH} = 15 Hz), 5.05 (vinyl H).

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(8) D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **37**, 881 (1954).

Synthesis of New Urethans. *p*-Ethylsulfonyl- and *p*-Dimethylsulfamoylcarbanilic Acid Esters

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Several *p*-arylsulfonylcarbanilic acid esters were reported to have antitumor activities.[1] New urethans listed in Table I were prepared by Curtius degradation of appropriate benzoyl azides.

The compounds proved to be inactive[2] (T/C = 89–102% at 400 mg/kg) against the L-1210 lymphoid leukemia in BDF_1 mice, and the Walker carcinosarcoma 256 in random-bred albino rats.

Experimental Section[3]

***p*-Ethylsulfonylbenzoyl Azide.**—*p*-Ethylsulfonylbenzoic acid ethyl ester (mp 64°) was prepared by known methods from *p*-ethylsulfonylbenzoic acid[4] and transformed to *p*-ethylsulfonylbenzoylhydrazide (mp 164°). This hydrazide (2.28 g, 0.01 mole) in 20 ml of 50% AcOH was stirred vigorously at ice bath temperature to give 2.27 g of azide (95%) mp 125° dec. *Anal.* ($C_9H_9N_3O_3S$) C, H, N.

p-Dimethylsulfamoylbenzoyl azide was prepared similarly from *p*-dimethylsulfamoylbenzoyl hydrazide[5] as a white powder (91%), mp 109° dec. *Anal.* ($C_9H_{10}N_4O_3S$) C, H, N.

(1) Al. Mavrodin, C. Demetrescu, and C. Chirita, *Rev. Roum. Chim.*, **10**, 1025 (1965).

(2) Screening results were supplied by CCNCS of the National Institutes of Health, Bethesda, Md.

(3) Melting points were taken on a Kofler hot stage microscope and were uncorrected. The ir spectra were determined with a Leitz model III spectrograph. Nmr spectra were obtained on a Varian A60A instrument.

(4) H. Sato, *Yakugaku Zasshi*, **72**, 74 (1952).

TABLE I

R	R'	Mp, °C	Yield, %	Formula[a]
Et	Et	135	89	$C_{11}H_{15}NO_4S$
Et	*t*-Bu	129	93	$C_{13}H_{19}NO_4S$
Et	*n*-Hexyl	109	95	$C_{15}H_{23}NO_4S$
Et	*n*-Octyl	124	88	$C_{17}H_{27}NO_4S$
Et	Allyl	121	86	$C_{12}H_{15}NO_4S$
Et	Benzyl	136	96	$C_{16}H_{17}NO_4S$
Et	Cholesteryl	222	92	$C_{36}H_{55}NO_4S$
Et	Cyclopentyl	142	79	$C_{14}H_{19}NO_4S$
Et	Cyclohexyl	139	83	$C_{15}H_{21}NO_4S$
Et	Cycloheptyl	120	85	$C_{16}H_{23}NO_4S$
Et	Cyclooctyl	127	79	$C_{17}H_{25}NO_4S$
Et	*o*-$MeOC_6H_4$	191	80	$C_{16}H_{17}NO_5S$
Et	Thymyl	143	84	$C_{19}H_{23}NO_4S$
Et	6-Allyl-4-$MeOC_6H_3$	154	73	$C_{19}H_{21}NO_5S$
Et	Ph_2CH	195	76	$C_{22}H_{21}NO_4S$
Et	α-Cyclohexyl-α-methylbenzyl	136	79	$C_{23}H_{29}NO_4S$
Et	*p*-Menth-3-yl	170	92	$C_{19}H_{29}NO_4S$
Me_2N	Et	127	71	$C_{11}H_{16}N_2O_4S$
Me_2N	*i*-Pr	159	76	$C_{12}H_{18}N_2O_4S$
Me_2N	*t*-Bu	169	78	$C_{13}H_{20}N_2O_4S$
Me_2N	*n*-Am	105	72	$C_{14}H_{22}N_2O_4S$
Me_2N	*n*-Hexyl	95	69	$C_{15}H_{24}N_2O_4S$
Me_2N	*n*-Octyl	107	68	$C_{17}H_{28}N_2O_4S$
Me_2N	Allyl	110	73	$C_{12}H_{16}N_2O_4S$
Me_2N	Cyclopentyl	170	86	$C_{14}H_{20}N_2O_4S$
Me_2N	Cyclohexyl	176	81	$C_{15}H_{22}N_2O_4S$
Me_2N	Cycloheptyl	170	83	$C_{16}H_{24}N_2O_4S$
Me_2N	Cyclooctyl	174	79	$C_{17}H_{27}N_2O_4S$
Me_2N	Benzyl	142	88	$C_{16}H_{18}N_2O_4S$
Me_2N	Cholesteryl	220	80	$C_{36}H_{56}N_2O_4S$
Me_2N	Ph_2CH	195	91	$C_{22}H_{22}N_2O_4S$
Me_2N	Ph_3C	132	65	$C_{28}H_{26}N_2O_4S$
Me_2N	Thymyl	155	78	$C_{19}H_{24}N_2O_4S$
Me_2N	*p*-Menth-3-yl	173	76	$C_{19}H_{30}N_2O_4S$
Me_2N	*o*-Methoxyphenyl	155	69	$C_{16}H_{18}N_2O_5S$
Me_2N	6-Allyl-4-$MeOC_6H_3$	193	70	$C_{19}H_{22}N_2O_5S$
Me_2N	α-Cyclohexyl-α-methylbenzyl	120	64	$C_{23}H_{30}N_2O_4S$

[a] All compounds were analyzed for C, H, N, and the results were satisfactory. Similarly ir and nmr spectra were as expected.

***p*-Ethylsulfonylcarbanilic Acid Benzyl Ester.**—*p*-Ethylsulfonylbenzoyl azide, (2.3 g, 0.01 mole) and 2.48 g (0.02 mole) of benzyl alcohol was refluxed for 1 hr in 20 ml of dry PhMe. The solvent was evaporated and the residue was recrystallized from dil EtOH to give 2.9 g (90%) of white plates, mp 136°. The other compounds listed in Table I were prepared in a similar way, except for the Et esters which were prepared by 3-hr refluxing of the appropriate azide in 10 times its weight of abs EtOH.

(5) H. Shirai, M. Yoneda, and N. Oda, *Nagoya Shiritsu Daigaku, Yakugakubu Kiyo*, **2**, 45 (1954); *Chem. Abstr.*, **50**, 11337 (1956).

Synthesis of 5,7-Dimethoxyindole[1]

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The predominance of the indole nucleus and its methoxy analogs in many biologically active systems

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