3.6 g. of partly-crystalline, neutral material, trituration of which with methanol afforded 0.4 g. of compound IV, identical with the compound obtained as described above by the same criteria.

1-Hydroxy-3-methyl-2-tetralylacetic acid (V). (*A*) Hydrogenation (40 lb.) of 1.0 g. of III in the presence of 1.2 g. of 10% palladium-charcoal in 200 ml. of ethyl acetate at 25° for 1.5 hr. gave 1.0 g. of colorless crystals, m.p. 135–138°. The infrared spectrum of this crude product was virtually identical with that of purified material (*vide infra*) and showed no lactone band. Recrystallization from cyclohexane–ethyl acetate raised the m.p. to 147–148°; the infrared spectrum (chf.) had broad, moderately intense absorption at 3.1–3.25 μ and an intense peak at 5.87 μ. The compound was soluble in sodium bicarbonate solution.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.75; H, 7.48.

(*B*) A suspension of III (1.0 g.) in 30 ml. of water was treated with excess sodium borohydride (*ca.* 4 g.) in portions, which resulted in solution of the compound. The solution was warmed on a steam cone for 1.5 hr., was chilled in ice, and was acidified slowly with cold hydrochloric acid. The product, after washing with cold water and drying in the air, was recrystallized from ethyl acetate; colorless crystals, m.p. 147–148°. The mixed melting point with V obtained as described above was not depressed, and the infrared spectra of the samples were identical.

1-Hydroxy-3-methyl-2-tetralylacetic acid lactone (VI). A pure sample of acid V was treated with 10% hydrochloric acid at 45° and the suspension was allowed to stand overnight at room temperature. The crystals were collected, washed with water, and air dried. The melting point of the crude lactone was 124–130°; the infrared spectrum showed a new, intense peak at 5.66 μ and no longer had bands at 3.1–3.25 or 5.87 μ. The compound was insoluble in sodium bicarbonate solution. Recrystallization from cyclohexane gave pure material, m.p. 135–136°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.18; H, 6.68.

3-Methyl-2-tetralylacetic acid (VII). Hydrogenation of 0.65 g. of III in the presence of 1.2 g. of 10% palladium-charcoal and 170 ml. of ethyl acetate at 80° and 40 lb. for 2 hours gave a quantitative yield of colorless crystals, m.p. 98–103°. Recrystallization from cyclohexane raised the m.p. to 107–109°. The infrared spectrum (chf.) had an intense peak at 5.87 μ.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.65; H, 7.81.

1-Hydroxy-3-methyl-3,4-dihydro-2-naphthylacetic acid lactone (VIII). A solution of 2.3 g. of III in 50 ml. of dry xylene was treated with 4 drops of benzenesulfonic acid, and the solution was refluxed under a water separator for an hour. The cooled solution was diluted with ether, was washed with 2 portions of sodium bicarbonate solution and 2 portions of water, and was dried over magnesium sulfate. Evaporation of the solvents gave 2.0 g. of bright yellow crystals. Trituration with ether afforded pale yellow crystals, m.p. 72–77°. Recrystallization from ether gave nearly pure material, m.p. 74–80°. The compound was somewhat contaminated with a persistent yellow impurity which could not be removed entirely. The infrared spectrum (chf.) showed a doublet, 5.57 μ (intense) and 5.70 μ (moderately-intense).

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.97; H, 6.04. Found: C, 77.26; H, 6.32.

A sample (2.2 g.) of III was melted *in vacuo* (1.0 mm.). The melt was refluxed at this pressure for 10 minutes, and was distilled. A few drops of orange distillate, b.p. 166–168° (0.8 mm.) were obtained before the remaining material decomposed, and this product crystallized rapidly. Recrystallization from ether gave pale yellow crystals, m.p. 79–83°. The infrared spectrum (chf.) of this material also had peaks at 5.56 and 5.70 μ and was virtually the same as the spectrum of material obtained as described above.

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Esters of *p*-Methyl- and *p*-Isopropylmandelic Acids as Mosquito Repellents

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In a previous paper[1] the preparation and mosquito repellent action of esters of mandelic acids were reported. Although substitution in the aromatic nucleus seemed to decrease the repellent effect of the esters against mosquitoes, further confirmation of this finding was sought.

TABLE I

ESTERS OF *p*-SUBSTITUTED MANDELIC ACIDS, R-C_6H_4-CHOHCOOR′

R′	n_D^{25}	B.P., °C./Mm.	Yield, %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
R = Methyl (yield based on *p*-tolualdehyde method E, ref. 1)							
Propyl	1.5055	157/12	30	69.21	69.19	7.75	7.51
Butyl	1.4999	162–6/13	48	70.05	70.18	8.10	8.11
Pentyl	1.4995	174/12	43	70.52	70.95	8.45	8.45
R = Isopropyl (yield based on *p*-isopropylmandelic acid method D, ref. 1)							
Methyl M.p. 81–82°C.		160–1/10	45	69.21	68.93	7.75	7.20
Ethyl M.p. 39–41°C.		166/10	60	70.24	69.91	8.16	7.92
Propyl	1.4938	174/10	62	71.16	71.23	8.53	8.35
Allyl	1.5118	177/10	53	71.77	71.58	7.74	7.58
Butyl	1.4955	182–3/10	61	71.97	71.96	8.96	8.54
Pentyl	1.4926	189–90/10	59	72.69	72.34	9.15	8.88
Hexyl	1.4918	201–2/10	66	73.34	73.37	9.41	8.73

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[1] W. F. Barthel, J. Leon, and S. A. Hall, *J. Org. Chem.*, 19, 485 (1954).

Ten new esters of *p*-methyl- and *p*-isopropylmandelic acid were prepared in order to study the effect of alkyl substitution in the aromatic nucleus on the mosquito repellent action. The esters were prepared as previously described, *p*-tolualdehyde and cuminic aldehyde being used as starting materials for the corresponding mandelic acids. Yields, physical constants, and analytical data are given in Table 1.

None of the esters exhibited any appreciable repellent effect against mosquitoes[2] although the corresponding unsubstituted mandelic esters have shown repellent action.[1]

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(2) Carroll N. Smith, I. H. Gilbert, H. K. Gouck, and others on the staff of the Orlando, Fla., laboratory conducted the repellency tests.

Ultraviolet Absorption Spectra of Nitrostyrene Derivatives[1]

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Although only scattered references to the ultraviolet spectra of nitroolefins are found in the literature, it appeared that the study of such spectra should allow assignment of stereochemical configuration particularly in the case of ω-nitrostyrene derivatives. The *trans*-ω-nitrostyrene system is characterized by a band of strong intensity in the region of 305–325 mμ, the exact position being affected by the nature of the substituent on the carbon atom bearing the nitro group.[2] The spectra of several nitrostyrene derivatives have been measured in alcohol solution and their characteristics are summarized in Table I.[3]

In each of the three *cis-trans* pairs examined, one of the isomers showed absorption beyond 300 mμ while the other did not. The compounds exhibiting absorption in the 300-mμ region have been assigned the *trans*-nitrostyrene structure. The alternative assignment of this long wave length absorption to the *trans*-stilbene system appears unattractive for the following reason: the α,α′-dinitrostilbene structures are known with certainty[4] and the isomer with the phenyl groups *cis* shows a definite absorption peak at 310 mμ while the *trans* isomer shows only end absorption in this region.[5]

TABLE I

SPECTRAL CHARACTERISTICS OF ω-NITROSTYRENE DERIVATIVES, $C_6H_5CR'{=}CRNO_2$

R	R′	M.P., °C.	λ_{max}	ϵ_{max}
cis-C_6H_5	NO_2	108–109	252 (sh)	7850
			310	4600
trans-C_6H_5	NO_2	187–188	238 (sh)	13300
cis-C_6H_5[a]	I	113–114	240	15200
			310	4400
trans-C_6H_5	I	176–177	242 (sh)	13700
			310	2300
trans-C_6H_5	H	127–128	281	21500
cis-C_6H_5	H	74–75	228	12200
			316	12100
H[b]	Cl	54–55	246 (sh)	8450
			285	5450
H	I	50–51	244 (sh)	14000
			284	9350
			310 (sh)	7750

[a] The intensities listed indicate only the extent of absorption at the wave lengths noted for comparison with the *trans* compound. *cis*-Nitroiodostilbene exhibited only end absorption with no definite peaks or shoulders. [b] The intensities previously reported for this compound [J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 1712 (1957)] are too low apparently due to partial decomposition of the material before the spectrum was measured.

The *cis* and *trans*-α-nitrostilbenes have been known for some time as products of the condensation of benzaldehyde and phenylnitromethane,[6] but little evidence as to their stereochemistry has been assembled.[7] It is known, however, that the lower melting isomer, which is now assigned a *trans*-nitrostyrene structure, is the more readily obtained and appears to be the thermodynamically more stable form. In this study the lower melting isomer was produced preponderently when either *meso* or DL-1,2-dinitro-1,2-diphenylethane was treated with pyridine.[8]

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

(3) In the table the designations *cis* and *trans* refer to the relation of the phenyl groups. It is clear that the *cis* compounds contain the *trans*-nitrostyrene system.

(4) K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, *J. Am. Chem. Soc.*, **75**, 2400 (1953).

(5) The spectra of the dinitrostilbenes as reproduced by Campbell *et al.*[3] appear to be in error as no maximum of an intensity comparable to those reported by them was found nor should one be expected of such a sterically crowded molecule. Since nitrostyrene derivatives partially decompose on standing, it is important that spectra are measured on freshly recrystallized samples. This point has been emphasized previously [M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **77**, 5696 (1955).]

(6) F. Heim, *Ber.*, **44**, 2016 (1911).

(7) B. Reichert and W. Kuhn, *Ber.*, **74B**, 328 (1941). These authors assigned the structures of some nuclear-substituted α-nitrostilbenes on the basis that the *cis* isomer had the lower melting point, the greater solubility and the more intense color. Their assignments are the same as ours.

(8) The use of sodium methoxide or piperidine to convert the 1,2-dinitro-1,2-diphenylethanes to α-nitrostilbenes also led to the lower melting isomer; see J. Meisenheimer and F. Heim, *Ann.*, **355**, 269 (1907); A. Angeli and L. Alessandri, *Atti. accad. Lincei*, **19**, I, 784 (1910) [*Chem. Abstr.*, **4**, 2634 (1910)].