allowed to stand for four days with occasional warming. Ice was next introduced to decompose excess hydride reagent and the reaction complex then hydrolyzed with dilute sulfuric acid. The ether layer was removed and the aqueous layer extracted with fresh ether. The combined ether extracts were then washed with water and extracted with dilute sodium carbonate solution to remove unreacted podocarpic acid. After drying over anhydrous potassium carbonate the ether solution was concentrated and hexane added. On cooling transparent cubes of podocarpinol crystallized out of solution; m. p. 177–178.5°. Recrystallization from ether gave 3.7 g. (56%) of pure material; m. p. 178–179°.

*Anal.*[8] Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.09; H, 9.08.

In an earlier run in which the total reaction time was two hours a yield of 4.6% of podocarpinol was obtained.

Methylation of podocarpinol with dimethyl sulfate in the usual manner gave O-methylpodocarpinol (m. p. 90–91°), first prepared by Campbell and Todd.[4] A mixed m. p. with the O-methylpodocarpinol prepared as described below showed no depression.

**O-Methylpodocarpinol** (V). (*a*) **From O-Methylpodocarpoyl Chloride (IV).**—Reaction between 33 g. of O-methylpodocarpoyl chloride (m. p. 61°) in 1 liter of ether and 10 g. of lithium aluminum hydride in 800 ml. of ether was carried out over a period of four days. The mixture was worked up in the same manner as described above (m. p. 91°) from which 28 g. (92%) of pure O-methylpodocarpinol was obtained after one crystallization from ether–hexane.

(*b*) **From Methyl O-Methylpodocarpate (III).**—Lithium aluminum hydride (8 g.) in 400 ml. of ether was treated with 15 g. of methyl O-methylpodocarpate m. p. 158–159° in 300 ml. of ether as above. From this experiment there was obtained 12.7 g. (93%) of O-methylpodocarpinol; m. p. 91°.

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(8) Analysis by Dr. Carl Tiedcke Microlaboratories, New York.

RIDBO LABORATORIES, INC.
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RECEIVED JANUARY 12, 1948

# NEW COMPOUNDS

## α-Nitrostilbene Analogs

The *alpha*-nitrostilbenes are physiologically active. Also compounds of the *alpha*, *beta*-diphenylethylamine type obtained by further reduction have been reported to have a selective effect in damaging sarcoma cells.[3]

Accordingly we have prepared nitro compounds of this type and submitted them to the National Cancer Institute for testing.

**1-α-Thienyl-2-phenyl-2-nitroethylene** was prepared by mixing 9.0 g. phenylnitromethane, 8.1 g. 2-thiophenealdehyde[4] and 3 ml. of a 10% solution of methylamine in methanol, warming gently, then shaking for three hours at room temperature. The bright yellow crystals which separated weighed 4.9 g. After triple recrystallization from absolute ethanol the product melted at 123° cor.

*Anal.* Calcd. for $C_{12}H_9O_2SN$: C, 62.34; H, 3.90; N, 6.06. Found: C, 62.45; H, 3.76; N, 6.06.

**1-α-Furyl-2-*o*-chlorophenyl-2-nitroethylene** was prepared by mixing 7.82 g. of *o*-chlorophenylnitromethane, 4.36 g. of freshly distilled furfural, and 5.16 cc. of a 16% solution of methylamine in methanol. The crystals which separated on standing three days weighed 3.96 g. The product was dissolved in absolute ethanol and the solution decolorized with activated carbon. After recrystallization from absolute ethanol the melting point was 101.1° cor.

*Anal.* Calcd. for $C_{12}H_8NO_3Cl$: C, 57.72; H, 3.21; N, 5.61. Found: C, 57.92; H, 3.12; N, 5.53.

**1-*m*-Nitrophenyl-2-phenyl-2-nitroethylene** was prepared by mixing 3 ml. of phenylnitromethane, 3.0 g. of *m*-nitrobenzaldehyde,[5] 0.5 ml. of 10% methylamine and 6 ml. of methanol. After standing four days the solution was diluted with 25 ml. of petroleum ether and chilled in Dry Ice. The yield of crystals was only 0.4 g. (7.5%). After recrystallization from absolute ethanol the melting point was 112.0° cor.

*Anal.* Calcd. for $C_{14}H_{10}N_2O_2$: C, 62.22; H, 3.70; N, 10.37. Found: C, 62.60; H, 3.75; N, 10.12.

**1-*p*-Nitrophenyl-2-phenyl-2-nitroethylene**, reported by Baker and Wilson[6] as melting at 155°, was prepared by us and found to melt at 157.5° cor., after repeated recrystallization.

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(2) Present address: Plough, Inc., Memphis, Tennessee.

(3) Shear, *et al.*, *Approaches to Tumor Chemotherapy*, American Association for the Advancement of Science, Washington, D. C. (1947), page 236 ff.; also Hartwell and Kornberg, THIS JOURNAL, **67**, 1607 (1946).

(4) Purchased from Arapahoe Chemicals, Inc., Boulder, Colo.

(5) Purchased from Eastman Kodak Company, Rochester, N. Y.

(6) Baker and Wilson, *J. Chem. Soc.*, 842–848 (1927).

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## 3-Chloro-6-methoxy-8-nitroquinoline

To a stirred mixture of 300 ml. of concentrated hydrochloric acid, 50.4 g. of 3-nitro-4-aminoanisole and 85.2 g. of arsenic acid, at 100°, there was added 30.0 g. of α-chloroacrolein during one hour. After an additional hour at 100°, the mixture was poured on ice. A solid which separated was filtered off and recrystallized from acetone; yield 16 g., m. p. 151–153°. Recrystallization from methanol raised the m. p. to 159.5–160°.

*Anal.* Calcd. for $C_{10}H_7ClN_2O_3$: C, 50.31; H, 2.94; Cl, 14.88; N, 11.74. Found: C, 50.68; H, 2.84; Cl, 15.06; N, 11.75.

The original aqueous filtrate gave no product on neutralization.

THE DIVISION OF MEDICINAL CHEMISTRY
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## New Compounds as Insect Repellents

The compounds listed in Table I were prepared as part of a project to discover new insect repellents.[1]

**2,2-Diethyl-1,3-Propanediol.**—A solution of 43 g. of potassium hydroxide in 400 ml. of 95% ethanol was added to an ice-cooled, well-stirred mixture of 167 g. of 38% formaldehyde solution and 100 g. of 2-ethylbutyraldehyde (Eastman Kodak Co.) at such a rate that the tem-

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(1) This work was performed under Contract NDCrc 136 between Harvard University and the Office of Scientific Research and Development, with Paul D. Bartlett as official investigator.