



*p*-Anisylmagnesium bromide was treated with ethyl pivalate to give 1,1-bis-(*p*-methoxyphenyl)-2,2-dimethylpropanol-1 (m. p. 81–83°. *Anal.* Calcd. for C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>: C, 75.97; H, 8.05. Found: C, 75.51; H, 7.84), which was then reduced over copper chromite to 1,1-bis-(*p*-methoxyphenyl)-2,2-dimethylpropane (II) m. p. 59–61°. *Anal.* Calcd. for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>: C, 80.24; H, 8.51. Found: C, 80.42; H, 8.55). This compound, more conveniently called 1,1-dianisylneopentane, is related to "methoxychlor" (III), the *p,p'*-dimethoxy analog of DDT, in the sense that the trichloromethyl group of "methoxychlor" has been replaced by a *t*-butyl group. The neopentane has insecticidal activity of the same order, although lower, as "methoxychlor." Some approximate LD 50 dosage ratios (1,1-dianisylneopentane: "methoxychlor") are as follows: German cockroaches (contact), 1:2; milkweed bugs (contact), 4:1; webbing clothes moth and carpet beetle larvae (wool impregnation), each 2:1; mosquito larvae (*A. aegypti*), 4:1; houseflies (spray), 4:1.<sup>1</sup> The tremors and paralysis characteristic of DDT and "methoxychlor" are produced by the neopentane. It has also been observed that the Ellenville strain of DDT-resistant houseflies is markedly more resistant to this compound than are ordinary strains of flies.<sup>2,3</sup>

The hypothesis of Martin and Wain,<sup>4</sup> that DDT toxicity is caused by hydrogen chloride release, obviously fails to explain the effectiveness of the chlorine-free product. Lauger's lipid-solubility hypothesis<sup>5</sup> and a possible relationship between steroids and DDT-type compounds<sup>6</sup> will be discussed in a later publication.

(1) Tests by the Wisconsin Alumni Research Foundation.

(2) Barber and Schmitt, *N. J. Agr. Exp. Sta. Bull.*, 742 (1948); Barber, Starnes and Starnes, *Soap and San. Chem.*, 24 [11] 120 (1948).

(3) We are greatly obliged to the staff of our Entomological Laboratory for certain of the biological tests reported above and to Mr. Ordway Starnes and the late Dr. George W. Barber of the Department of Entomology, Rutgers University, and N. J. Agr. Exp. Station for tests with resistant strains of flies.

(4) Martin and Wain, *Nature*, 154, 512 (1944).

(5) Lauger, Martin and Mueller, *Helv. Chim. Acta*, 27, 892 (1944).

(6) Lauger, Pulver, Montigel, Weismann and Wild, "Mechanism of Intoxication of DDT Insecticides in Insects and Warm-Blooded Animals," Lecture, Washington, D. C., July 31, 1945, Geigy Company Inc., New York, N. Y., 1946.

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#### CITRIC ACID FORMATION BY *ASPERGILLUS NIGER* THROUGH CONDENSATION OF 3C<sub>2</sub> MOIETIES

Sir:

Biogenesis of citric acid *via* condensation of oxalacetate and acetate (C<sub>4</sub> dicarboxylic acid + C<sub>2</sub>) is a reasonably well-accepted hypothesis. The C<sub>4</sub> dicarboxylic acid is generally presumed to originate *via* the Wood-Werkman reaction (pyruvate and carbon dioxide), though now the C<sub>2</sub>

condensation must also be considered.<sup>1</sup> The following experiments were intended to demonstrate the relative participation of the two modes of genesis of the C<sub>4</sub> moiety.

Radioactive citrate was produced from sucrose by washed *Aspergillus niger* submerged mycelium (200 mg. dry wt.) in the presence of 2 mg. of high specific activity methyl-C<sup>14</sup>-labeled acetate and carbon dioxide containing 19.2 atom % C<sup>13</sup>O<sub>2</sub>. To the 38 mg. of citric acid produced in forty hours (at which time considerable unconsumed sucrose remained) carrier citric acid (350 mg.) was added; calcium citrate was isolated and purified by precipitation and twofold reprecipitation from hot solution.

The radioactive citric acid was converted to pentabromoacetone, which represents the non-carboxyl carbons of the citric acid. The non-carboxyl carbons were also obtained in the form of acetone, by dilute acid-dichromate oxidation of another portion of citric acid. The acetone was further degraded to iodoform and acetic acid; the acetic acid was then degraded<sup>2</sup> to methylamine and carbon dioxide. Specific activity measurements were made on barium carbonate obtained by wet combustion.

TABLE I  
C<sup>13</sup> AND C<sup>14</sup> VALUES

Fraction	Specific activity <sup>a</sup>	Atom % C <sup>13</sup>
1 Total citric acid	0.16	1.107 ± 0.005 <sup>c</sup>
2 Non-carboxyl carbons		
Pentabromoacetone	.15	1.084 ± 0.002 <sup>c</sup>
Acetone	.15	
Iodoform	.17	
Acetic acid	.16	
Methylamine	.15	
Carbon dioxide	.17	
3 Carboxyl carbons		
Primary carboxyls	.12	1.132 ± 0.009 <sup>c</sup>
Secondary carboxyl	.16	1.090 ± 0.010 <sup>c</sup>
4 CO <sub>2</sub> in atmosphere		
Initial	.00	19.2 ± 0.1
Final	.43 <sup>b</sup>	10.5 ± 0.1

<sup>a</sup> Counts/sec./mg. BaC<sup>14</sup>O<sub>3</sub> (measured on citrate diluted with carrier). <sup>b</sup> Measured as 4.3 counts/sec./mg. BaC<sup>14</sup>O<sub>3</sub>, but calculated as if diluted same amount as the citrated. <sup>c</sup> Measurements made on citrate diluted with carrier, and its degradation products.

The mean C<sup>13</sup> content of the atmospheric carbon dioxide (19.2 + 10.5/2 = 14.9 atom %) enables one to calculate that CO<sub>2</sub>-carbon from the atmosphere entered citrate to the extent of 1.3% of the total citrate carbon; if the Wood-Werkman reaction were entirely responsible for net citrate synthesis, the figure should be 16.7%. Unlabeled intracellular carbon dioxide from sucrose theoretically could also account for some net synthesis; we have been unable to conceive a definitive experiment on this point. On the other hand,

- (1) Foster, *et al.*, *Proc. Natl. Acad. Sci., U. S.*, 35, 668–672 (1949).  
(2) Phares, to be published.