noticeable melting point range suggests that there is still some impurity present or that the product is not a single isomer. *Anal.* Found: F, 55.7, 56.0; Cl, 20.0. Calcd. for $C_6F_{10}Cl_2$: F, 57.0; Cl, 21.3. The literature values reported for this compound are: b.p. 107.5–107.7°; m.p. 12–14°; n^{20}_D 1.3413.[3]

The compound or compounds containing approximately twelve carbon atoms per molecule have thus far been obtained only in small amounts and have not been identified. The fraction does decolorize neutral permanganate and can be chlorinated photochemically, indicating olefinic character.

Some preliminary kinetic data indicate that, in general, the acid takes part in reactions at room temperature in the presence of Lewis-type bases both in aqueous and nonaqueous media. The decomposition in water may be considered as an example of this general type of reaction which the acid will undergo.

Acknowledgment.—We would like to thank Dr. H. M. Scholberg and Mr. E. A. Kauck of the Central Research Department of Minnesota Mining & Manufacturing Company for supplying the fluorocarbon acid.

---

[3] V. V. Lindgren and E. T. McBee, U. S. Patent 2,480,081, August 23, 1949; *C. A.*, **44**, 2020g (1950).

FLUORINE LABORATORIES
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA.

RECEIVED MARCH 17, 1951

Isolation of Tomatidine from the Roots of the Rutgers Tomato Plant

BY NORMAN G. BRINK AND KARL FOLKERS

Tomatidine, the nitrogenous aglycone of the antifungal agent tomatine, has been isolated directly from the roots of the Rutgers tomato plant (*Lycopersicum esculentum* (L.) Mill., horticultural variety "Rutgers").

The isolation of crystalline tomatine from the dry leaves of the Red Currant tomato, *L. pimpinellifolium*, was described by Fontaine, Irving, Ma, Poole and Doolittle.[1] The isolation of tomatine from the leaves of six species of wild tomato plants was reported by Kuhn, Löw and Gauhe[2] who cited yields of the crystalline product from the dried plant material which varied from 0.5 to 5%, the highest yield being obtained from *L. esculentum var. pruniforme*. They stated that tomatine could not be isolated from the commonly cultivated tomato plants; and that in those plants which did contain it, the amount of tomatine present decreased significantly in September and October.

Acid hydrolysis of crystalline tomatine gave xylose, galactose, two moles of glucose,[3] and a nitrogenous aglycone, tomatidine.[1,2] Recent work[4,5] has shown that tomatidine is a steroid secondary amine, for which the molecular formula $C_{27}H_{45}NO_2$ was proposed. Kuhn, Löw and Gauhe,[2] however, indicated formulas for tomatine and tomatidine containing two less hydrogen atoms.

We wish to report the isolation of tomatidine hydrochloride directly from the roots of the Rutgers tomato plant, a horticultural variety of *L. esculentum* (L.) Mill. developed by L. G. Schermerhorn at the New Jersey Agricultural Experiment Station, and distributed generally about 1934. The plants were gathered during the fall of the year, after the fruit had been picked, and only the washed and dried roots were used in the extraction. The extract was divided into a number of fractions, one of which gave a crystalline product in low yield (*ca.* 0.01%), which after purification was identified as tomatidine hydrochloride. The low yield may be explained partly by the isolation procedure, which included no deliberate acid hydrolytic step; and partly by the fact that the plants were gathered at the time when their tomatine content might be expected[2] to be low.

It is of interest that our analytical results on purified tomatidine hydrochloride are in agreement with the composition $C_{27}H_{45}NO_2$[4,5] rather than $C_{27}H_{43}NO_2$.[2]

Experimental[6]

In a typical extraction procedure, 1.36 kg. of dried root material was moistened with water and then extracted in a Soxhlet apparatus for 24 hours with 15 l. of methanol. The extraction was then continued for an additional three days, using fresh methanol. The combined methanolic solutions were concentrated *in vacuo* to a volume of 300 ml., and to this aqueous solution another 300 ml. of water was added, and the *p*H was adjusted to 8 with sodium hydroxide. After standing with occasional stirring for several days, the mixture was extracted with eight 1-l. portions of ether. The combined ethereal extracts were evaporated and the residue triturated with 2.5 l. of ether. After removal of solids, the ethereal solution was washed with eight 250-ml. portions of very dilute sodium hydroxide solution (*p*H 10); and then it was extracted with eight 250-ml. portions of 0.06 *N* hydrochloric acid. On standing in the cold, the acidic solution deposited crystalline material which was collected by filtration, washed with water, and dried. It weighed 183 mg.

The product, after two recrystallizations from ethanol melted at 275–280° (dec.); $[\alpha]^{25}_D$ $-8.8 \pm 2.1°$ (*c*, 0.455 in methanol).

Anal. Calcd. for $C_{27}H_{45}NO_2 \cdot HCl$: C, 71.73; H, 10.26; N, 3.10; Cl, 7.84. Calcd. for $C_{27}H_{43}NO_2 \cdot HCl$: C, 72.05; H, 9.86; N, 3.11; Cl, 7.88. Found: C, 71.76, 71.41; H, 10.26, 10.23; N, 3.50; Cl, 7.83.

Treatment of the recrystallized hydrochloride in methanolic solution with silver oxide, and recrystallization of the product from aqueous ethanol gave the free base, m.p. 204–205°. When this material was admixed with a sample of authentic tomatidine[7] for which we observed the m.p. 205–207°, no depression of the melting point occurred.

---

[1] T. D. Fontaine, G. W. Irving, Jr., R. Ma, J. B. Poole and S. P. Doolittle, *Arch. Biochem.*, **18**, 467 (1948).

[2] R. Kuhn and I. Löw, *Ber.*, **81**, 552 (1948); R. Kuhn, I. Löw and A. Gauhe, *ibid.*, **83**, 448 (1950).

[3] R. M. Ma and T. D. Fontaine, *Arch. Biochem.*, **27**, 461 (1950).

[4] T. D. Fontaine, J. S. Ard and R. M. Ma, THIS JOURNAL, **73**, 878 (1951).

[5] Y. Sato, A. Katz and E. Mosettig, *ibid.*, **73**, 880 (1951).

[6] The authors wish to thank Mr. John Madas for technical assistance. They are indebted to Mr. Richard N. Boos and his associates for the microanalyses.

[7] Kindly furnished by Dr. T. D. Fontaine.

RESEARCH LABORATORIES
MERCK & CO., INC.
RAHWAY, N. J.

RECEIVED MARCH 30, 1951

Some Derivatives of 2- and 3-Methylthiophene

BY TOD W. CAMPBELL AND WARREN W. KAEDING

In view of recent reports by various workers on the halogenation of methylthiophenes with N-bromosuccinimide[1a,b,2] we feel that it would be worthwhile to record some of our experimental observations on this reaction, carried out prior to the ap-

---

[1] (a) E. Campaigne and W. M. Le Suer, THIS JOURNAL, **70**, 415, 1555 (1948); (b) K. Dittmer, R. P. Martin, W. Herz and S. J. Cristol, *ibid.*, **71**, 1201 (1949).

[2] J. Le Cocq and Buu-Hoi, *Compt. rend.*, **224**, 658 (1947).