

sisted for a long time in these solutions. It seems quite likely, therefore, that in the very dilute solutions the isothiocyanate decomposed too quickly to have any effect on the fish, while in the concentrated solutions the undissolved layers served as a reserve which kept benzoyl isothiocyanate in solution long enough to kill the goldfish. The fish which were killed by this compound bled from their gills, sometimes severely, and even those which did not die appeared inflamed about the gills.

At the higher concentrations, the toxicity of phenyl thiocyanate was very close to that of benzoyl isothiocyanate. Its decrease in toxicity became appreciable at a higher concentration than did that of benzoyl isothiocyanate, but the curve of Fig. 2 is regular, and results can be duplicated throughout its length. Phenyl thiocyanate is quite stable toward water. The goldfish were intensely irritated very quickly by this compound. They swam about violently, and often tried to jump out of the water.

p-Thiocyanogeno-*N*-dimethylaniline was very similar to phenyl thiocyanate in toxicity at all concentrations tested. It did not seem to irritate the fish as much as phenyl thiocyanate.

Summary

The toxicity to goldfish of certain organic thiocyanates and isothiocyanates has been determined at several concentrations, and the results are presented in the form of survival-time curves.

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[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND STATION OF THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TWO CONSTITUENTS OF PAROSELA BARBATA (OERST.) RYDB.¹

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Two constituents have been isolated from the leaves and stems of *Parosela barbata* (Oerst.) Rydb. in connection with the examination of certain plants reported to contain fish poisons.

The first, a white crystalline solid melting at 84–84.5°, was shown to be montanyl alcohol. This compound is assigned the formula C₂₉H₆₀O by Damoy,² who obtained the alcohol from beeswax. Gascard and Damoy³ report the melting point of montanyl alcohol as 84°. Damoy² gives the melting point of its acetate as 68–68.2° and that of its iodide as 64–64.2°.

On the other hand, Fargher and Probert⁴ report montanyl alcohol ob-

¹ Collected by Dr. H. Pittier in Caracas, Venezuela, and identified by Dr. S. F. Blake, Bureau of Plant Industry, Washington, D. C.

² Damoy, *J. Pharm. Chim.*, **29**, 225–236 (1924).

³ Gascard and Damoy, *Compt. rend.*, **177**, 1442–1443 (1923).

⁴ Fargher and Probert, *J. Textile Inst.*, **15**, 337–346T (1924).

tained from the wax of American cotton as $C_{28}H_{58}O$ with a melting point of 83.5° and the melting point of its acetate as $67-67.5^\circ$.

The material isolated in this investigation was purified by repeated recrystallizations from chloroform until the melting point showed no further rise. The alcohol crystallizes from chloroform or benzene in colorless, diamond-shaped plates. It is very slightly soluble in cold solvents but is very soluble in warm chloroform or benzene. The highest yield of fairly pure substance was 0.075% of the plant and our total supply consisted of about 3.0 g.

Molecular weight determinations by the method of Landsberger⁵ with chloroform as solvent gave values of 415, 412 and 385. By the method of Karl Rast⁶ values of 410 and 387 were obtained.

The acetate of the material melted at $68-69^\circ$ and the iodide melted at $64-64.5^\circ$. The phenylurethan was prepared and found to have a melting point of 96° . This derivative does not seem to have been prepared by previous workers.

It is not possible to distinguish positively between two compounds possessing formulas of $C_{28}H_{58}O$ or $C_{29}H_{60}O$ by means of carbon and hydrogen analysis due to the small difference in carbon and hydrogen content. There is, however, a difference of 0.62% in the iodine content of the two corresponding iodides, and analyses gave values which varied only 0.04 and 0.11% from the value calculated for $C_{29}H_{59}I$. This is in agreement with the formula for montanyl alcohol determined by Damoy.

The second constituent, a yellow oil, was obtained by steam distillation of the substance remaining after evaporation of the methyl alcohol mother liquor of the montanyl alcohol. The yield amounted to 0.6% of the plant material.

The oil boiled between 95 and 110° at 4-5 mm. pressure. Its density and refractive index were: d_{20}^{20} 0.947, and n_D^{20} 1.497. It possessed a peculiar sickening odor and was insoluble in water, but readily soluble in organic solvents. It added bromine readily and decolorized neutral permanganate solution but did not reduce Fehling's solution.

At a concentration of 1:10,000 at 27° it killed goldfish in an average of 117 minutes.⁷ Four fish were used to obtain this value. The toxicity tests were carried out by the method described by Gersdorff.⁸

Experimental

Isolation of Montanyl Alcohol.—720 g. of the ground plant was extracted for two and a half hours in a Soxhlet extractor with benzene. The benzene was then dis-

⁵ Landsberger, *Ber.*, **31**, 458 (1898).

⁶ Karl Rast, *ibid.*, **55**, 1051 (1922).

⁷ For toxicity of the acetone extract of the entire plant, see Drake and Spies, *J. Ec. Entomol.*, **25**, No. 1, 129-133 (1932).

⁸ Gersdorff, *THIS JOURNAL*, **52**, 3440 (1930).

tilled off and the residue dissolved in boiling methyl alcohol and filtered on a hot water funnel. On cooling a gelatinous, green, pasty mass separated, which was filtered off with suction. This solid was stirred up with cold ether, which removed much of the color. The ether was filtered off, the solid dissolved in warm chloroform and the solution decolorized with charcoal. The chloroform solution was allowed to cool slowly and to stand for some time, whereupon it deposited a crystalline material which was further purified by repeated recrystallizations from the same solvent. A brownish color may persist even after this treatment, but it can be removed by a crystallization from methyl alcohol, followed by recrystallization from chloroform again; yield, 0.55 g. of substance melting at 82.5°. Recrystallization from chloroform to constant melting point gave a product melting at 84–84.5°.

Anal. Subs., 2.948, 2.919 mg.: CO₂, 8.813, 8.772; H₂O, 3.759, 3.687. Calcd. for C₂₃H₃₃O: C, 81.86; H, 14.24. Calcd. for C₂₂H₃₀O: C, 81.98; H, 14.25. Found: C, 81.53, 81.96; H, 14.17, 14.04.

Acetylation of Montanyl Alcohol.—0.15 g. of montanyl alcohol was treated with 2 cc.⁹ of acetic anhydride containing a trace of sulfuric acid and kept on a boiling water-bath for one hour. Methyl alcohol was then added cautiously, and after destruction of the excess acetic anhydride the acetate crystallized from the methyl acetate-methyl alcohol mixture. The ester was recrystallized once more from methyl alcohol and melted at 68–69°.

Anal. Subs., 3.659, 3.262 mg.: CO₂, 10.680, 9.498; H₂O, 4.315, 3.901. Calcd. for C₃₀H₆₀O₂: C, 79.56; H, 13.36. Calcd. for C₃₁H₆₂O₂: C, 79.75; H, 13.39. Found: C, 79.60, 79.40; H, 13.10, 13.29.

Preparation of Montanyl Iodide.—0.09 g. of montanyl alcohol was treated with 0.025 g. of red phosphorus and 0.3 g. of iodine and the whole kept at a temperature of 80–90° for three and a half hours. The mixture was then extracted with warm chloroform and the chloroform solution washed with a dilute aqueous solution of sodium bisulfite. It was then washed with water and finally dried over calcium chloride. The chloroform was evaporated off and the solid residue recrystallized to constant melting point from ether. It melted at 64–64.5°.

Anal. Subs., 4.999, 3.205 mg.: CO₂, 11.856, 7.623; H₂O, 4.976, 3.207. Calcd. for C₂₈H₅₇I: C, 64.57; H, 11.04. Calcd. for C₂₉H₅₉I: C, 65.12; H, 11.13. Found: C, 64.67, 64.86; H, 11.06, 11.12. Subs., 6.907, 7.222 mg.: AgI, 3.052, 3.182. Calcd. for C₂₈H₅₇I: I, 24.39. Calcd. for C₂₉H₅₉I: I, 23.77. Found: I, 23.88, 23.81.

Preparation of the Phenylurethan of Montanyl Alcohol.—0.04 g. of montanyl alcohol and two drops of phenyl isocyanate were refluxed for half an hour in benzene solution. The crystals which separated on cooling were recrystallized once from benzene. The compound melted at 96°.

Anal. Subs., 2.874, 3.080 mg.: CO₂, 8.385, 8.971; H₂O, 3.136, 3.319. Calcd. for C₃₅H₆₅O₂N: C, 79.32; H, 11.99. Calcd. for C₃₆H₆₇O₂N: C, 79.48; H, 12.05. Found: C, 79.38, 79.41; H, 12.12, 11.97.

Summary

1. Montanyl alcohol has been isolated from *Parosela barbata* and identified by means of several of its derivatives.
2. The phenylurethan of montanyl alcohol has been prepared.
3. The formula of montanyl alcohol suggested by Damoy has been confirmed.

⁹ This was sufficient to effect complete solution at 100°.

4. An oil possessing some toxicity to goldfish has been isolated and described.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

A REACTION BETWEEN DIETHYL ETHER AND PHOSPHORUS PENTACHLORIDE

BY WALTER S. GUTHMANN¹

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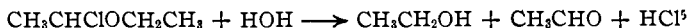
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In the course of some work on molecular rearrangements in the triphenylmethylhydroxylamine series, it was found necessary to reflux ether solutions of the materials being studied with phosphorus pentachloride for several days. At the end of this time water was added to the reaction mixture, and a very considerable and unexpected evolution of acetaldehyde was observed. This led to the investigation reported here.

Liebermann and Landshoff² report the formation of a crystalline compound of the probable formula $C_8H_{14}O_2P_3Cl_{15}$, when ether is treated with phosphorus pentachloride, and show that it is not a direct addition product with the formula $(C_4H_{10}O)_2 \cdot 3PCl_5$. No mention is made, however, of the evolution of acetaldehyde upon addition of water to the above compound.

Reactions of phosphorus pentachloride with aliphatic-aromatic ethers have been reported.³ In these cases only the aromatic portion of the molecule is oxidized.

It has been found that halogens, at ordinary temperatures, will react with ether to form α -halogen ethyl ethers which are easily hydrolyzed by water:⁴



It is well known that phosphorus pentachloride may be used as a chlorinating agent, and this fact might well account for the reaction described below, except that some organic phosphorus derivatives are formed at the

¹ A portion of the dissertation submitted to the graduate faculty of the University of Chicago, by W. S. Guthmann, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Liebermann and Landshoff, *Ber.*, **13**, 690 (1880).

³ Henri, *ibid.*, **2**, 710 (1869); Colson, *Compt. rend.*, **99**, 975 (1884).

⁴ Richter, "Organic Chemistry," P. Blakiston's Son and Co., Philadelphia, 1922, Vol. I, p. 129.

⁵ Since this paper was written, Henze and Murchison [*THIS JOURNAL*, **53**, 4077 (1931)], have reported the preparation of α -chloroethyl *n*-alkyl ethers by saturating equimolar quantities of paraldehyde, and the alcohol which contains the desired alkyl group, with hydrogen chloride, in the cold. The products hydrolyze very readily to re-form the original materials; on long standing they polymerize and leave a dark tarry residue.