SYNTHESIS OF DIETHYLAMIDES OF FATTY ACIDS
BY A CATALYTIC METHOD AND A STUDY
OF THEIR REPELLENT ACTIVITY

A. V. Starkov, V. I. Katunina, V. P. Dremova, and G. G. Gerasimova

Together with diethyltoluamide, which is widely used at present, diethylcaprylamide has been patented comparatively recently as an effective repellent [1].

The results of studies carried out in our institute showed that diethylcapramide and diethyllauramide also possess good repellent properties [2, 3]. A mixture of diethylamides prepared from an industrial fatty acid fraction containing 7 to 9 carbon atoms proved no less active. The basic method of preparing the amides of the various acids was the so-called two-stage acid chloride method.

A catalytic method of amidating acids by passing a mixture of diethylamine and acid over a water-removing catalyst at 250-300°C also presented interest [4, 5].

The individual fatty acids which we used were commercial products of the Novocherkassk synthetic products factory. Caproic and caprylic acids corresponded to TU-GKh No. 1530-61; and capric acid, to MRTU 6-09-2521-65. The C₇-C₉ industrial fatty acid fraction was a yellowish liquid which boiled at 150-190°C/100 mm. Technical diethylamine was preliminarily distilled, bp 55-56.5°C.

Bead silica gel, brand VTU-8-61, served as catalyst. Study of the catalytic method was carried out in a flow system, in the usual laboratory set-up. As reactor we used a glass tube (Pyrex) 50 cm long and 28-30 mm in diameter. In the middle part of the tube practically along its whole length was located a thermocouple well. The reaction tube was set in an electric furnace with a controllable heater.

Bead-form catalyst with granule size 5 mm, in an amount of 50 ml, was placed in the temperature plateau zone in the middle part of the tube, and the remaining space was filled with ceramic rings. The feedstock was fed in with the aid of a dispenser (design of the Institute of Organic Chemistry of the Academy of Sciences of the USSR). A graduated glass syringe of 100 ml volume served as a capacity. The rate of product feed was varied with the aid of pulleys of various diameters, such that the contact time was 4 to 20 sec.

On exit from the apparatus, reaction products were cooled and condensed in a system of reflux condensers. The diethylamine was stripped from the product obtained, the residue was dissolved in benzene or toluene, and washed with water until all the diethylamine salt of the fatty acid had been removed. The diethylamide of the corresponding acid was distilled under vacuum after removal of the solvent.

Synthesis of the diethylamides was conducted at 300°C. An increase in temperature over 300°C leads to disproportionation of the diethylamine. Dropping the temperature below 300°C is inexpedient, to avoid condensation of the starting acids on the catalyst.

The synthesis of diethylcaprylamide was studied at five different molar ratios of diethylamine to caprylic acid (from 1.05 to 6 to 1). In preparing the diethylamides of the remaining acids, we used three ratios - 4 : 1, 2 : 1, and 1.2 : 1.

The dependence of yield of fatty acid diethylamides on contact duration at various molar ratios of starting components is shown in Fig. 1. Contact duration was calculated from the formula

\[
\tau = \frac{M_{\text{diu}} \cdot 273 - 3600}{v \gamma (273 + t) \cdot 22400},
\]

Dependence of yield of fatty acid diethylamides on duration of contact at various molar ratios of starting components. 

- Yield of diethylamide (in %);
- $\tau$ = contact time (in sec);
- $M_{av}$ = mean molecular weight of mixture; $v_f$ = feed rate of original feedstock (in liters per liter of catalyst per h);
- $\gamma$ = density of mixture (in g/ml); $t$ is temperature in reaction zone (in degrees).

An increase in molar ratio of diethylamine to caprylic acid from 1.05 to 6 leads to an increase in yield of diethylcaprylamide of 30-40%. For all the acids studied, a change in molar ratio from 1.2 to 4 gives a yield increase of desired product of 20-30%. An increase in contact duration of the reacting components in the interval studied also leads to a marked increase in yields of fatty acid diethylamides.

Here the molecular weight of the starting acid hardly affects the yield of diethylamide, which is confirmed in the case of amidating the C7-C9 fatty acid fraction.

The catalytic method of synthesizing fatty acid diethylamides is characterized by rather high yields of the desired products. Thus, at a molar ratio of diethylamide to acid equal to 2 or 4, and a contact time of the order of 15-20 sec, the yield of diethylamides attains, respectively, 80 to 90%, based on starting acid. The one-stage nature of the process, simplicity of apparatus design, absence of an additional corroding component, and high yield of desired products make the direct acid amidation process very promising for industry.

Biological evaluation of the repellents synthesized was carried out under laboratory conditions [6] with respect to X. cheopis fleas at 18-20°C and under field conditions with respect to mosquitoes, principally of genus Aedes.

In the first selection tests, at a dose of active operating substance (AOS) of 1 ml per m² of white sheeting, diethylamides of the C7-C9 fatty acid fraction, caprylic and capric acid proved to be the strongest repellents. At an AOS dose of 40 ml per m² on the first day after treatment all the tested diethylamides had satisfactory repellent activity (coefficient of repelling action, 100-82%); the most prolonged repellent action (over the course of 55 days) was maintained by the diethylamide of the C7-C9 acid fraction, caprylic and capric acids; sheeting treated with diethylcaproamide became practically nonrepellent after the 55th day.

Under field conditions, observations were conducted in a period of average temperature 18-25°C, relative humidity 45-65%, at an infestation intensity of 3035 mosquitoes (mostly Aedes excrucians, Aedes vexans, and Aedes communis) in a 3-min recorded period. Alcoholic solutions of the preparations were applied to the skin of the forearm in an amount of 0.5-1 ml. Dimethyl phthalate was the standard. The greatest term of protective action (2-3 h) was established for a 30% alcoholic solution of diethylcaprylamide or the diethylamides of the C7-C9 acids, which were only slightly less active than diethyltoluamide. Under these conditions, the duration of dimethyl phthalate action was 2-2.5 h.

A fine-drop spray from an aerosol cylinder containing diethylcaprylamide permitted application of a small amount of the preparation on the costume. After 15 min of treatment, the consumption of aerosol mixture was 11-12 g, or 2.7-3.0 g of preparation per 1 m² of treated clothing. The duration of protective action did not exceed five days. On treatment of cloth on the basis of 30 ml of AOS per m² satisfactory repellent action was maintained for 15 days. Addition of dimethyl phthalate permitted extending the term of protective action of the diethylamides on fabrics. On treatment with mixtures of the diethylamides and dimethyl phthalate in the ratio 2:3, the term of repellent action was increased to 25-30 days; dimethyl phthalate without addition of diethylamides ensured protection for 10-15 days.

**LITERATURE CITED**