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RICININE AND ITS TRANSFORMATIONS

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Ricinine was isolated from Ricinus communis *L. Its derivatives were obtained.*

Key words: *Ricinus communis,* alkaloid, ricinine.

Seeds of common castor (*Ricinus communis* L., Euphorbiaceae) are used mainly to produce castor oil (Oleum ricini) [1, 2].

Pulp defatted by benzene that contains the toxic protein ricin is thermally deactivated to provide livestock feed. The alkaloid ricinine remains in industrial pulp after ricin is detoxified.

Ricinine ($C_8H_8O_2N_2$) was first isolated from castor seeds in 1864 [3].

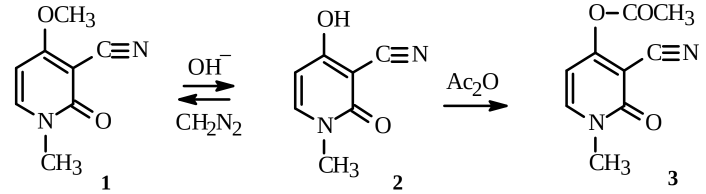
The toxic protein ricin-T was isolated from seeds of middle-asian *Ricinus communis* and its primary structure was determined [4].

Pulp remaining after extraction of castor oil is extracted with alcohol. Evaporation and extraction with $CHCl_3$ gives ricinine. Its content in defatted seeds is 0.1%; in industrial pulp, 0.08%.

Ricinine (**1**), $C_8H_8O_2N_2$, mp 200-201°C. Mass spectrum: M^+ 164 (100%). It sublimes in vacua without decomposition and forms a crystalline salt with mercuric chloride.

The IR spectrum (cm^{-1}) of **1** contains absorption bands for N-methyl (2958 and 2854), nitrile (2224), and lactam carbonyl (1662).

Alkaline hydrolysis of **1** forms **2**, so-called ricininic acid [3], $C_7H_6O_2N_2$. Mass spectrum: M^+ 150 (10%). The IR spectrum (cm^{-1}) of **2** contains bands for hydroxyl (3047), N-methyl (2637 and 2264), nitrile (2221), and lactam carbonyl (1661).



Ricininic acid is very soluble in bases. Methylation with diazomethane produces ricinine. The phenolic hydroxyl is poorly acetylated with acetic anhydride. We first prepared the O-acetyl derivative **3**, $C_9H_8O_3N_2$. Mass spectrum: M^+ 192 (100%). The IR spectrum (cm^{-1}) of **3** contains bands for N-methyl (3099 and 3057), nitrile (2234), ester (1778), and lactam carbonyl (1666).

EXPERIMENTAL

The solvent systems $CHCl_3$—*n*-butanol—CH_3CO_2H (25:10:1) (1) and *n*-butanol—CH_3CO_2H—H_2O (30:20:1) (2) were used.

TLC was performed on Silufol UV-254 plates. Compounds were visualized in UV light.

Mass spectra were obtained in an MS-25 RF (Kratos) instrument using direct sample introduction, accelerating

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potential 4 kV, and ionizing potential 70 V. IR spectra were recorded on a Perkin—Elmer System 2000 FT-IR Fourier spectrometer in KBr pellets.

Isolation of Ricinine. Ground castor seeds (2.4 kg) were extracted on standing with acetone at room temperature. The yield of oil after evaporation of acetone was 1 kg or 40% of the dry mass.

Defatted seeds were extracted with ethanol (85%). The ethanol was evaporated in vacua. The extract stratified into two layers. The upper oil layer and lower aqueous layer were washed with ether, made basic with aqueous ammonia, and repeatedly extracted with $CHCl_3$. The $CHCl_3$ extract was dried over anhydrous sodium sulfate. The solvent was evaporated. The solid crystals (2.1 g, 0.08%) are technical-grade ricinine.

Ricinine (1). Crystals are whitish-cream colored, mp 200-201°C (ethanol), R_f 0.20 (rosy spot) for TLC using system 1.

Mass spectrum, *m/z*: 164 (M^+) (100%), 146, 135, 121, 96, 93, 80, 69, 58, 51.

Mercuric Salt of Ricinine. Ricinine (0.14 g) was dissolved in warm distilled water (10 mL) and treated with mercuric chloride solution (0.1%). The mercuric salt of ricinine precipitated. The precipitate was separated and recrystallized from aqueous ethanol to give the mercuric salt of ricinine (0.08 g), mp 202-203°C.

Preparation of 2 from 1. Ricinine (**1**, 0.35 g) was dissolved in aqueous NaOH (10 mL, 5%), heated on a boiling-water bath for 30 min, cooled, and acidified with H_2SO_4 (5%). The precipitated white, fine, needlelike crystals (0.31 g) were recrystallized from ethanol, mp 286-288°C (dec.), R_f 0.40 for TLC on Silufol using system 2.

Methylation of Ricininic Acid by Diazomethane. Ricininic acid (200 mg) was dissolved in dry methanol (65 mL), treated with diazomethane in ether (50 mL), and left in a refrigerator for 48 h. The solvent was evaporated. The solid was dissolved in $CHCl_3$ (50 mL), washed with NaOH solution (2%), and dried over anhydrous Na_2SO_4. The solvent was evaporated. The solid ricinine was recrystallized from ethanol, mp 200-201°C, yield 120 mg.

Preparation of O-Acetylricininic Acid. Ricininic acid (3.4 g) was treated with acetic anhydride (15 mL) and boiled on a sand bath for 6 h. The reaction mixture crystallized entirely upon cooling. The crystals were vacuum filtered, washed with acetic anhydride, and dried to give O-acetylricininic acid (3.35 g), mp 154-155°C (acetone). Mass spectrum, *m/z*: 192 (M^+), 164, 148, 147, 121, 95, 84, 82, 66, 64.

Quantitative Determination of Ricinine in Castor Pulp. Ground pulp (30.0 g) was exhaustively extracted with ethanol in a Soxhlet apparatus for 7-8 h. The ethanol extract was condensed to 50-60 mL and basicified with ammonia. Ricinine was repeatedly extracted with $CHCl_3$ in a separatory funnel (500-600 mL). The $CHCl_3$ solution was shaken 5-6 times with H_2SO_4 (20 mL, 2%).

The acidic extract was basicified with ammonia and again extracted with $CHCl_3$. The $CHCl_3$ extract was dried over anhydrous Na_2SO_4 and evaporated on a water bath. The solid is technical ricinine, yield 0.07% of the pulp mass, R_f 0.20 for TLC on Silufol using system 1.

REFERENCES

1. Kh. Kh. Kholmatov, I. A. Kharlamov, P. K. Alimbaeva, M. O. Karriev, and I. Kh. Khaitov, *Principal Medicinal Plants of Middle Asia* [in Russian], Meditsina, Tashkent (1984).
2. D. A. Murav′eva, *Pharmacognosy* [in Russian], Meditsina, Moscow (1991).
3. A. P. Orekhov, *Chemistry of Alkaloids* [in Russian], Moscow (1955).
4. D. A. Khashimov, Kh. G. Alimov, and P. Kh. Yuldashev, *Khim. Prir. Soedin.*, 243, 845 (1988).