Triphenylbromomethane reacts with metallic magnesium far more readily than the chloride, and gives rise to triphenylmethylmagnesium bromide. This has been isolated in crystalline state and analyzed.

The formation of triphenylmethylmagnesium bromide takes place in two successive stages: (a) formation of triphenylmethyl; (b) formation, from that, of the magnesium compound, $2\ R_3C + Mg + MgX_2 = 2\ R_3CMgX$. The formation of the triphenylmethyl is in itself most probably the result of two successive reactions: $R_3CX + Mg = R_3CMgX$; $R_3CMgX + R_3CX = 2\ R_3C + MgX_2$.

The formation of triphenylmethylmagnesium halide from triphenylmethyl and the system $Mg + MgX_2$ lends much support to the hypothesis that the action of the binary system is through the intermediate formation of the active compound MgX.

ANN ARBOR, MICHIGAN

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

TOXICAROL. A CONSTITUENT OF THE SOUTH AMERICAN FISH POISON CRACCA (TEPHROSIA) TOXICARIA[1]

BY E. P. CLARK

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In connection with a survey of fish poisoning plants as sources of insecticides now in progress in this Laboratory, a chemical examination of the roots of *Cracca* (*Tephrosia*) *toxicaria* was made.[2] It was shown that this plant material contains a crystalline substance which in high dilutions is toxic to fish. The crude crystals had a greenish-yellow color and a melting point of 200–203°. Closer examination revealed that the material was composed of at least two substances. The one that occurs in much the greater proportion is a bright canary yellow, optically inactive compound which has a melting point of 219° (corr.). It has the molecular formula $C_{23}H_{22}O_7$ and has one hydroxyl and two methoxyl groups. The name *toxicarol* has been assigned to it.

The second substance is a pale green crystalline compound which is separated from toxicarol only with difficulty. Owing to the small quantity of the plant available it was impossible to obtain sufficient crystalline material to carry the fractionation of the second substance to a state of certain analytical purity. Its optical properties, however, were readily determined, and from these data it was shown that the substance was identical with an optically inactive dimethoxy compound having the formula $C_{23}H_{22}O_6$ which is found in *Derris* and *Cube* roots.

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[1] The name *Tephrosia* Pers. is antedated by *Cracca* and under the American code of Botanical Nomenclature all species of *Tephrosia* should bear the generic name *Cracca*.

[2] The material was received from the Department of Agriculture, Georgetown, British Guiana, through the American Vice Consul, Harold R. Brown.

It is of interest to note that the molecular formula for toxicarol differs from the formula of rotenone by one oxygen atom only, whereas the formula for the second compound is identical with that of rotenone. Furthermore, both substances have two methoxyl groups, as does rotenone, and both are approximately as toxic to fish. These considerations, together with the fact that all three substances are found in *Derris*, indicate that possibly some common structural relationships exist among the three bodies. Further work, now in progress, is expected to throw more light upon this matter.

Experimental

Fifty grams of the ground roots of *Cracca toxicaria* were completely exhausted with ether. The resulting extract, after the removal of the solvent, was dissolved in 30 cc. of hot methanol and then made alkaline with 10 cc. of an aqueous 5% sodium hydroxide solution. The mixture was immediately heated to its boiling point, causing a tarry substance to separate. The supernatant liquid was decanted, diluted with three volumes of water, made acid to congo red with sulfuric acid and extracted with chloroform. The chloroform extract was washed with water, dried with sodium sulfate, filtered and evaporated to a small volume. Several volumes of methanol were then added to the concentrate and the solution was evaporated to a volume of approximately 10 cc. Upon allowing the liquid to cool, crystallization began at once. The yield was 0.65 g. or 1.3% of the drug taken. As stated before, the product had a greenish-yellow color and a melting point of 200–203°.

Pure toxicarol was obtained from this material by dissolving the crude crystals in hot chloroform, filtering the solution through norite, again heating the solution to its boiling point and then adding about 12 volumes of boiling alcohol. The solution was maintained in a state of vigorous boiling until it became practically free from chloroform, at which time toxicarol began to crystallize. The process was soon completed, and the crystals were filtered from the boiling liquid. The product thus obtained had a melting point of about 215°. Two or three recrystallizations of this material by the method just given resulted in a product having a constant melting point of 219° (corr.). It consists of bright, greenish-yellow, six-sided plates and rods whose refractive indices are: n_α, 1.580 (frequent); n_β, 1.618 (common); and n_γ, >1.768, all ± 0.003. In parallel polarized light with crossed nicols the extinction is inclined and the elongation is negative. Double refraction is very strong. Many of the plates are so thin that only first order white and yellow colors are shown. Frequently plates remain bright in all positions when the stage is rotated. In convergent polarized light with crossed nicols the large plates show distinct biaxial interference figures with a large axial angle. The optic sign is positive.[3]

Anal. Calcd. for $C_{23}H_{22}O_7$: C, 67.30; H, 5.41; CH_3O (2), 15.1. Found: C, 67.09; H, 5.41; CH_3O, 15.3.

Toxicarol Benzoate.—Two cc. of benzoyl chloride was added to a solution of 2 g. of toxicarol in 20 cc. of hot pyridine. After an hour the reaction mixture was poured into 300 cc. of water, causing the separation of an oil. This was removed from the mother liquor by decantation and dissolved in 75 cc. of boiling alcohol. Upon cooling, 1.5 g. of toxicarol benzoate, having a melting point of 200°, separated. This was recrystallized

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[3] The optical data recorded in this communication were determined by George L. Keenan of the Food, Drug and Insecticide Administration of the U. S. Department of Agriculture. Appreciation is acknowledged for this valuable coöperation.

from its solution in chloroform by the addition of 5 volumes of methanol. It separated in rosets of fine colorless needles whose melting point was 202° (corr.). The yield was 1.35 g. Its refractive indices are n_α, 1.590; n_β, indeterminate; n_γ, 1.702. An intermediate value n_i, 1.650, is also common. In parallel polarized light with crossed nicols the extinction is inclined and the sign of elongation is positive.

Anal. Calcd. for $C_{30}H_{26}O_8$: C, 70.01; H, 5.10; CH_3O (2), 12.06. Found: C, 69.68; H, 5.05; CH_3O, 12.28.

The Second Compound, $C_{23}H_{22}O_6$.—The mother liquors from the first purification of toxicarol were evaporated to dryness in vacuo, and the residue was dissolved in about 25 cc. of boiling alcohol and filtered. The filtrate, upon cooling, deposited a small crop of crystals having a light greenish-yellow color and a melting point of about 180°. Upon repeated fractional crystallization the melting point of the substance was reduced to 173°, and its color became much lighter, but there was insufficient material to resolve the substance to a state of certain analytical purity. Its crystallographic properties, however, were readily determined to be as follows. The compound crystallized in rods, many of them six-sided in outline. Their refractive indices are n_α, 1.570; n_β, 1.590 (common); and $n_\gamma > 1.739$, all ± 0.003. The extinction is inclined, and the elongation is negative. Most of the crystals do not extinguish sharply when examined in parallel polarized light with crossed nicols.

These properties are the same as those possessed by a substance obtained from *Derris* and *Cube* roots. This material will be reported upon shortly, when it will be shown to be an optically inactive dimethoxy compound $C_{23}H_{22}O_6$, whose melting point is 171°. A mixture of this compound and the second substance obtained from *Cracca toxicaria* melted at 172°. This and the fact that the two substances have the same optical properties prove that they are identical.

The two substances from *Cracca toxicaria* have been shown to be decidedly toxic to fish. For example, at a dilution of 1–20,000,000 at 27°, goldfish weighing approximately 2 g. were killed by toxicarol in four and one-half hours and by the $C_{23}H_{22}O_6$ compound in three hours, while rotenone given for comparative purposes, was effective in two and one-fourth hours. These toxicological data, determined by W. A. Gersdorff of the Insecticide Division of the Bureau of Chemistry and Soils, were taken from a series of experiments which will be reported in detail elsewhere. They are recorded at this time, however, to show the relative toxicity of the substances under consideration.

Summary

1. Two active fish poisons have been isolated from the roots of *Cracca toxicaria.*

2. One of these, toxicarol, predominates. It is an optically inactive compound, $C_{23}H_{22}O_7$, possessing one hydroxyl and two methoxyl groups.

3. The second substance is an optically inactive dimethoxy compound having the molecular formula $C_{23}H_{22}O_6$.

4. It has been indicated that both substances occur in *Derris* while the $C_{23}H_{22}O_6$ compound has been found also in *Cube* roots.

5. Toxicarol kills goldfish in a dilution of 1–20,000,000 at 27° in four and one-half hours. The $C_{23}H_{22}O_6$ compound at the same dilution and temperature is lethal in three hours.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE FIFTH PENTA-ACETATE OF GALACTOSE, ITS ALCOHOLATE AND ALDEHYDROL

BY M. L. WOLFROM

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In the work herein reported, the methods employed in the synthesis of the crystalline free aldehyde form of glucose[1] have been extended to galactose, and we have obtained this form of galactose penta-acetate and also its crystalline hydrate and ethyl alcoholate. This penta-acetate is of particular interest because it adds a fifth isomer to the series of four already known. Erwig and Koenigs[2] prepared the first form, m. p. 142°, of galactose penta-acetate. This beta ring form was isomerized to the alpha form of the same ring structure by Hudson and Parker[3] on heating with acetic anhydride and zinc chloride. Hudson[4] then reported a third form found in small yield in the acetylation mother liquors from the preparation of the first form. This was prepared in larger quantity by Hudson and Johnson[5] and isomerized to the fourth form by the acetic anhydride and zinc chloride reaction. These four forms were found by Hudson to conform in rotation to two alpha and beta pairs of two different ring structures and constituted the first proof, based on the isolation of crystalline derivatives, that a sugar could exist in more than one lactal or ring structure. The third form of galactose penta-acetate has been prepared in higher yield by a method recently reported by Schlubach and Prochownick.[6] The properties of the five forms of galactose penta-acetate are shown in Table I.

TABLE I

PROPERTIES OF THE FIVE PENTA-ACETATES OF GALACTOSE

Form	M. p., °C.	$[\alpha]_D$ $CHCl_3$,[a] U. S. P.
First galactose penta-acetate, β-form	142	+ 23.0
Second galactose penta-acetate, α-form	96	+107.0
Third galactose penta-acetate, β-form	98	− 42.0
Fourth galactose penta-acetate, α-form	87	+ 61.0
Fifth galactose penta-acetate, μ-form	121	− 25 (Initial)

[a] The first four forms were measured at 20°, the fifth at 26°.

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[1] M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

[2] E. Erwig and W. Koenigs, *Ber.*, **22**, 2207 (1889).

[3] C. S. Hudson and H. O. Parker, THIS JOURNAL, **37**, 1589 (1915).

[4] C. S. Hudson, *ibid.*, **37**, 1591 (1915).

[5] C. S. Hudson and J. M. Johnson, *ibid.*, **38**, 1223 (1916).

[6] H. H. Schlubach and Vilma Prochownick, *Ber.*, **62**, 1502 (1929).