[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Rotenone. XXX. The Non-Crystalline Constituents of Derris Root[1]

BY H. L. HALLER AND F. B. LAFORGE

When derris or cubé root is extracted with a suitable organic solvent, and the solution is concentrated, most of the rotenone present separates in crystalline form.

The uncrystallizable residue, freed from the greater part of the rotenone, which is obtained by complete evaporation of the solvent is found to be approximately as toxic as rotenone itself when tested against fish.[2,3]

This non-crystalline material contains large quantities of deguelin[4] and toxicarol, which have never been obtained from it by direct crystallization. When an alcoholic solution of the resinous material is made slightly alkaline, deguelin and toxicarol separate as an optically inactive crystalline mixture, which by suitable manipulation can be separated into the two components.[5] (Tephrosin is also present, but it is probably formed by air oxidation of deguelin.) As they are difficultly soluble in most solvents and crystallize especially well, it is not possible that they can be present in the resinous material in the state in which they have been isolated.

Crystalline rotenone, deguelin, and toxicarol are almost insoluble in petroleum ether. However, when derris root is extracted with this solvent a large proportion of all these constituents is dissolved together with other substances. On concentration of the petroleum ether extract, there results a white amorphous material containing much deguelin and toxicarol together with rotenone, but relatively less of the by-products than are found in the residues obtained by extraction with other solvents. This material is especially suitable for the investigation of the uncrystallizable constituents. It can be freed from toxicarol by extracting its ethereal solution with dilute alkali. The resulting "deguelin concentrate" was used in the experiments described.

Takei has devised a method for the quantitative estimation of deguelin and rotenone in non-crystalline plant residues.[2] We have applied this method to the alcoholic mother liquor obtained after separation of the crystalline inactive deguelin from the deguelin concentrate and have shown that it contains more of the same compound.

We have also applied a colorimetric method developed by C. R. Gross and C. M. Smith of this division for the quantitative estimation of deguelin and rotenone in plant extracts.[6] The results obtained by this method were in substantial agreement with those found by direct isolation of deguelin and the dehydro compounds. The former shows that the deguelin very strongly predominates, while the latter does not indicate the relative proportion of deguelin and rotenone.

Takei has also reported[2] the isolation of optically active deguelin, m. p. 166 $[\alpha]_{\mathrm{D}} -23°$, from derris resin.

We were unable to obtain the crystalline active compound from our concentrate in spite of its high deguelin content (over 50%).

When a concentrated alcoholic solution of the deguelin concentrate was seeded with the purported *l*-deguelin furnished by Takei, the substance failed to induce crystallization. This material melted as reported, but on recrystallization it melted at 171°, and it showed no appreciable rotation. On comparison of the material with an authentic sample of inactive deguelin by optical examination of the crystals, no differences were detectable. We surmise that his substance consisted of inactive deguelin that contained a small quantity of rotenone.

It has been shown that the β-dihydrorotenone obtained by ring closure of isodihydrorotenone

---

(1) Rotenone XXIX, THIS JOURNAL, **56**, 1620 (1934).

(2) Takei, Miyajima and Ono, *Ber.*, **66**, 1826 (1933).

(3) Various comparative tests of derris extractives and rotenone, many of them unpublished, have been made by the Bureau of Entomology, U. S. Dept. of Agriculture. It has been shown that rotenone is not the only important constituent of these extractives. For example, Jones *et al.* [*J. Econ. Ent.*, **26**, 451 (1933)] found that powdered extract of derris which contained about 25% of rotenone was as toxic to mosquito larvae as pure rotenone and Campbell *et al.* [*Soap*, **10**, 81 (1934)] found that kerosene extract of a sample of derris from which no rotenone could be isolated was effective against house flies. It follows that toxic substances other than rotenone must be present in derris extractives. It was thought that deguelin and toxicarol might be responsible for the results just mentioned, but tests of these compounds against aphids by Davidson [*J. Econ. Ent.*, **23**, 877 (1930)], against silkworms by Shepard and Campbell [*ibid.*, **25**, 142 (1932)], and against mosquito larvae by Campbell and Sullivan (unpublished) indicate that toxicarol is practically non-toxic and that deguelin is less toxic than rotenone.

(4) The quantity is in excess of the rotenone in most samples of derris root. Takei, Miyajima and Ono, *loc. cit.*

(5) Clark, THIS JOURNAL, **53**, 313 (1931).

(6) Gross and Smith, *J. Off. Agr. Chem.*, **17**, 336 (1934).

(*dl*-rotenonic acid) is identical with dihydrodeguelin.[2,7] It follows then that the β-dihydrorotenone[8] obtained from active rotenonic acid would be identical with active dihydrodeguelin.

As this compound crystallizes well from alcoholic solution, it would be expected to separate from a hydrogenated solution of material containing considerable amounts of free active deguelin. Therefore the deguelin concentrate was hydrogenated and an alcoholic solution of the reduced material seeded with β-dihydrorotenone prepared from optically active rotenonic acid. In this manner optically active dihydrodeguelin was readily obtained. The yield was equal to about 35% of the deguelin found by other methods in the material employed, showing that at least a corresponding amount of free optically active deguelin was present. It is hardly possible that more free deguelin is present and that the dihydro derivative fails to crystallize because of the presence of impurities, for it has been demonstrated by experiment that when one part of active dihydrodeguelin is dissolved in twenty parts of methyl alcohol containing 1.5 parts of unhydrogenated deguelin concentrate, more than 90% of the added dihydrodeguelin separates.

It is possible, however, that part of the active dihydrodeguelin may be present in the hydrogenated material in a form with a configuration on the asymmetric carbon atoms different from that of the known dihydro compound, and which does not crystallize,[9] but is racemized to an inactive crystalline form.[10] It is also possible that part of the deguelin is present in the amorphous material in combination with another substance.

Whichever may be the correct interpretation, an additional quantity of dihydrodeguelin about equal to the first is obtained by the employment of alkali, but the compound so isolated is inactive. The mother liquor from the last crystallization still contains one-fourth of the total dihydrodeguelin, which can be isolated as its dehydro compound.

As shown, the deguelin concentrate contained at least 19% of free optically active deguelin and an additional 25% of deguelin which may have been active. If the toxicity of active deguelin is markedly greater than that of inactive deguelin, the high toxicity of extracts of derris that are poor in rotenone may be more readily understandable. The relative toxicity of active and inactive deguelin is not known, but the active and inactive dihydrodeguelins have been tested by Campbell and by Fink against mosquito larvae (results unpublished), and the active form has been found decidedly more toxic than the inactive. The former is also more toxic than rotenone at the concentrations tested. It is therefore probable that active deguelin would be more toxic than inactive deguelin.

The probably optically active toxicarol contained in the uncrystallizable crude residues may also contribute to their toxicity.

Experimental Part

Preparation of Active Deguelin Concentrate.—Two kilograms of ground derris root[11] was extracted repeatedly in a percolator at ordinary temperature with petroleum ether (b. p. 30–60°), about 20 liters being used to exhaust the material. The product obtained after removal of the solvent, consisting of 81.5 g. of nearly white amorphous residue, was dissolved in about 1.5 liters of ether, and the solution was repeatedly extracted with 5% aqueous potassium hydroxide solution until no substance was dissolved. Three and a half grams of the difficultly soluble potassium salt of toxicarol separated from the aqueous solution during the extraction and was removed by filtration. The aqueous solution was then acidified, causing the separation of about 16 g. of material, which consisted largely of impure toxicarol. The total quantity of material removed by alkali treatment was therefore about 19.5 g.

The ethereal solution containing the material insoluble in alkali was dried and concentrated to about 300 cc. After several days of standing in the ice box it deposited 8 g. of rotenone melting at 163°. After removal of the solvent from the ethereal solution, a nearly colorless amorphous residue was obtained, representing the remainder of the extracted material. This product, which has been designated as "deguelin concentrate," was the material used in the investigations described.

A 2% chloroform solution rotated in a 2-dm. tube −2.1°, $[\alpha]^{20}_{D}$ −52°. A 4% benzene solution rotated in a 2-dm. tube −8.1°, $[\alpha]^{20}_{D}$ −101°. As indicated by tests on goldfish and mosquito larvae, the material has about the same toxicity as has rotenone.

All attempts to induce crystallization by the use of solvents were unsuccessful. When a concentrated alcoholic solution of the material was seeded with crystals supplied

---

(7) Clark, THIS JOURNAL, **54**, 3000 (1932).

(8) Haller, *ibid.*, **53**, 733 (1931); **54**, 2126 (1932).

(9) It has been shown that the isomerism of the two known rotenolones is due to different arrangement of the substituents on the same asymmetric carbon atom, combined perhaps with geometrical isomerism in other groups. The same type of isomerism exists among the isorotenolones and hydroxydeguelins.[1]

(10) We have prepared an inactive form of isorotenone by alkali treatment, and acetyl isorotenone on saponification yields an isorotenone possessing a rotation different from that of the usual form. (The details are given in the experimental part.)

(11) The sample employed was analyzed by the carbon tetrachloride extraction method of Jones [*Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 23 (1933); *J. Wash. Acad. Sci.*, **23**, 36 (1933)]. The quantitative data reported in this article apply only to this particular sample, which contained 0.9% rotenone and 9.4% total extract.

by Takei and purporting to be active deguelin, only a small quantity of crystalline material separated. This, however, proved to be rotenone.

Isolation of Inactive Deguelin from Deguelin Concentrate.—Eight and nine-tenths grams of the concentrate was dissolved by warming in 50 cc. of methyl alcohol in a stoppered flask provided with tubes arranged for the displacement of the air. Hydrogen was then passed through the apparatus for a suitable length of time, after which ten drops of 40% potassium hydroxide solution was introduced through a tube. The solution was warmed from time to time to prevent separation of the dissolved material until crystallization had begun. After three or four hours, 10 additional drops of 40% alkali was added, and the flask was closed and allowed to stand for about thirty-six hours. The deposited crystalline material was removed by filtration, and after washing and drying melted at 160–166°. The yield was 3.4 g. or 38.2% of the material employed. After recrystallization it melted at 170–173° and was shown to be deguelin by comparison with an authentic sample by the optical immersion method. It was optically inactive.

The alcoholic mother liquor, which was found to be neutral to litmus, together with the alcoholic washings, was concentrated under reduced pressure, the residue dissolved in ether, and the solution was agitated with two 15-cc. portions of 2% potassium hydroxide solution. On acidification and extraction with ether the alkaline solution yielded a trace of resinous material which gave a phenol test with ferric chloride.

The ethereal solution of the alkali-insoluble fraction yielded on evaporation 4.5 g. of light-colored residue. Four grams of this material was dissolved in 60 cc. of 95% ethyl alcohol, 10 drops of 40% potassium hydroxide solution was added and the mixture was exposed to a current of air for three hours. The volume of the solution decreased to 40 cc. but no separation of material occurred. Five grams of sulfuric acid in 10 cc. of alcohol was added, and the solution was boiled under reflux for two hours. After standing overnight, the separated crystalline material was filtered off, washed and dried. It weighed 1.4 g., which corresponds to 1.6 g. for the 4.5 g. of residue obtained.

The separated crystalline material was essentially a mixture of dehydrorotenone and dehydrodeguelin. It was separated by Takei's method and found to consist principally of dehydrorotenone, as indicated by the large proportion of alkali-soluble material obtained after hydrogenation. This material did not crystallize completely, however, and therefore no exact statement can be made as to the proportions of the two dehydro compounds present.

In previous experiments at this stage, we have observed the presence in small amounts of an unidentified crystalline substance. The new compound, which is difficult to isolate, crystallizes in triangular prisms. When a small quantity was finally obtained by the use of mixtures of chloroform and methyl alcohol and the substance was recrystallized, it consisted of heavy tetrahedrons melting at 240–250°. It analyzed for a compound of formula $C_{19}H_{14}O_6$.

Anal. Calcd. for $C_{19}H_{14}O_6$: C, 67.43; H, 4.16; CH_3O, (2) 18.33. Found: C, 67.54; H, 4.22; CH_3O, 17.63.

The acid mother liquor from the dehydro compounds was diluted and extracted with ether, and the solution was washed with water and dried. The residue weighed 2.5 g. It was redissolved in ether and extracted with dilute alkali, which removed about 0.5 g. of dark-colored material. After proper dilution an aliquot of the 2 g. of ether residue was tested with fish and found to possess only insignificant toxicity.

The total amount of deguelin plus rotenone, as represented by the deguelin and dehydrodeguelin plus dehydrorotenone isolated, was thus found to be 3.4 + 1.6 = 5.0 g. or 56.2% of the material used.

Colorimetric Estimation of Deguelin Plus Rotenone in the Deguelin Concentrate.—Application of the colorimetric method of Gross and Smith to the original deguelin concentrate showed a total deguelin plus rotenone content of 60–63%, which is in substantial agreement with the figure (56.2%) obtained by isolation of deguelin and the dehydro compounds. When analyzed by the colorimetric method, an aliquot from the 4.5 g. of residue that corresponded to 1.6 g. of dehydrodeguelin plus dehydrorotenone (35.5%) showed a deguelin–rotenone content of 31–35%. Finally, the 2 g. of residue obtained after removal of the remaining deguelin and rotenone as the dehydro derivatives showed by the colorimetric method a deguelin–rotenone content of about 4%.[12]

Isolation of Optically Active and Optically Inactive Dihydrodeguelin from the Deguelin Concentrate.—Eight and nine-tenths grams of deguelin concentrate in about 100 cc. of ethyl acetate was shaken in a hydrogen atmosphere with 0.3 g. of platinum oxide catalyst. After four hours, 530 cc. of hydrogen had been absorbed, more than half of which was taken up in the first hour. The solution was filtered, the solvent removed under reduced pressure, the residue dissolved in ether, and the solution was extracted with dilute aqueous alkali.

The alkaline solution was acidified and extracted with ether. The residue obtained after removal of the solvent crystallized partly on standing, and the crystalline material when recrystallized from methyl alcohol melted at 213°. It was identified by optical examination of the crystals as tetrahydrorotenone (dihydrorotenonic acid). The yield was 0.5 g. of pure substance.

The solvent was removed from the ethereal solution of the alkali-insoluble main fraction, and the residue was dissolved in about 100 cc. of methyl alcohol. This solution was seeded with optically active β-dihydrorotenone (dihydrodeguelin) and allowed to stand at room temperature for several days. The deposited crystalline material was removed by filtration and treated with butyl ether, which removed a small quantity of amorphous material. It was then washed with petroleum ether and dried. The yield was 1.7 g. The product which melted at 155–156° was identified by optical comparison with an authentic sample as active β-dihydrorotenone (dihydrodeguelin), and when the two substances were mixed the melting point was not lowered.

A 4% solution in benzene rotated in a 2-dm. tube $-8.30°$, $[\alpha]^{20}_{D}$ $-104°$. This rotation is slightly higher than that found for the β-dihydrorotenone obtained by

---

[12] We are indebted to C. R. Gross for making these determinations.

ring closure of optically active isodihydrorotenone. A 4% solution of the latter substance in benzene rotated in a 2-dm. tube −7.40°, $[\alpha]^{20}_D$ −92.5°. Because in the process of its isolation the isodihydrorotenone had been in contact with alkali, a slight racemization may have occurred. The higher rotation found for the compound isolated from the hydrogenated deguelin concentrate is probably the correct value for pure dihydrodeguelin. The yield of 1.7 g. corresponds to 19.1% of the deguelin concentrate. Therefore at least this proportion of free active deguelin was originally present in the material.

The mother liquor, from which the active dihydrodeguelin had been removed, was concentrated to about 40 cc., the air in the flask was displaced by hydrogen, and 10 drops of 40% potassium hydroxide was added. Crystallization began after one hour, after which 10 drops more of the alkali was added, and the flask was closed and allowed to stand overnight The crystalline material was washed with methyl alcohol and dried. The yield was 1.3 g. After recrystallization the product melted at 170–173° after it had begun to soften at 153°. It was identified by comparison of the crystals with authentic material as inactive β-dihydrorotenone (dihydrodeguelin). It showed no rotation in 4% benzene solution in a 2-dm. tube.

The total quantity of active plus inactive dihydrodeguelin isolated was 3.0 g. After addition of 15 drops of 40% alkali the mother liquor from the inactive dihydrodeguelin was exposed to a current of air for two hours. The volume of the solution (then about 25 cc.) was made up to 40 cc. by addition of 15 cc. of ethyl alcohol containing 4 g. of sulfuric acid, and the solution was boiled for two hours under reflux. On standing overnight, 1.0 g. of dehydrodihydrodeguelin was deposited. After recrystallization it melted at 262–265° as recorded for this compound.

The total amount of crystalline material isolated from 8.9 g. of material, represented by 1.7 g. of active, 1.3 g. of inactive, dihydrodeguelin, 0.5 g. of tetrahydrorotenone and 1.0 g. of dehydrodihydrodeguelin originating from the deguelin and rotenone in the concentrate, was 4.5 g., or 50.5%.

In an effort to determine whether any of the deguelin (possibly in its enol form) was associated with a volatile acid, the deguelin concentrate was treated with dilute alkali, and the water-soluble material obtained was acidified and subjected to steam distillation. The result was negative.

It is certain that some form of cleavage of substances present in the material under discussion is caused by the action of the alkali, but efforts to isolate definite products were only partly successful. The alcoholic filtrate, obtained after isolation of inactive deguelin as described previously, was freed from the solvent, the residue dissolved in ether, and the water-soluble material removed by washing. The residue was then subjected to long-continued distillation at 0.001–0.01 mm. and 120° in a Hickman-type still. The small quantity of a colorless oil thus obtained analyzed after redistillation for a compound of formula $C_{30}H_{64}O_5$, with one methoxyl and one hydroxyl group. When the temperature was raised to 180°, part of the resin itself distilled and was obtained as a white amorphous solid. Analysis of this material indicated a formula of $C_{32}H_{38}O_7$ with two methoxyl groups. Owing to the doubtful purity of both the oil and the solid obtained after alkali treatment, no great importance can be attached to these formulas. When distilled under the same conditions the original material yielded no oil.

Conversion of Optically Active Isorotenone into the Inactive Form.—Two grams of isorotenone was dissolved in 60 cc. of boiling 95% alcohol in a hydrogen atmosphere. Twelve drops of 40% potassium hydroxide in 10 cc. of alcohol was added through the condenser, and boiling was continued for one and a half hours. The solution was then acidified and concentrated to 40 cc. About one gram of crystalline material was obtained. It was washed with alcohol and water and recrystallized from alcohol. It melted at 170–171° and the crystals showed the same optical properties as isorotenone. The compound was optically inactive.

Saponification of Acetylisorotenone.—A solution of 0.5 g. of acetylisorotenone[13] in 30 cc. of 95% alcohol containing 3 g. of sulfuric acid was boiled for two hours under reflux. The crystalline material which separated on standing was removed and recrystallized from methyl alcohol. It melted at 170–171°. A 3.86% benzene solution in a 2-dm. tube rotated −1.63°, $[\alpha]^{20}_D$ −21.1°. For comparison the rotation of isorotenone was made in the same solvent. A 4% benzene solution rotated in a 2-dm. tube −5.97°, $[\alpha]^{20}_D$ −74.6°. A dioxane solution of isorotenone was dextrorotatory; a 4% dioxane solution in a 2-dm. tube rotated +1.04°, $[\alpha]^{20}_D$ +13°.

Summary

The insecticidal action of extracts of derris root is due not only to rotenone but also to other constituents which remain in the uncrystallizable residues. These residues, from which optically inactive deguelin and toxicarol have been obtained, are the subject of the present investigation.

The material extracted from derris root by petroleum ether has a higher concentration of the known toxic compounds than have extracts made with other solvents.

The material so obtained can be freed from toxicarol by alkali extraction of its ethereal solution. The resulting product is strongly optically active and contains about 50% of deguelin as indicated by colorimetric estimation and by isolation of the inactive form, but no crystalline active deguelin can be obtained from it.

By catalytic hydrogenation of the material, the active deguelin present is converted into a corresponding active dihydro derivative, part of which separates from a methyl alcoholic solution in crystalline form. Most of the remaining dihydrodeguelin can be isolated by conversion into

---

[13] Smith and LaForge, THIS JOURNAL, **54**, 2996 (1932).

the inactive form by alkali treatment. It is probable that some deguelin is also present in the residues in an active form but having a configuration different from that of the isolated crystalline compound. That part of the active deguelin exists in some form of combination is not excluded. No toxic compound other than rotenone, deguelin and toxicarol has been found in the residues.

WASHINGTON, D. C. RECEIVED JULY 2, 1934

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Catalytic Hydrogenation of Amides to Amines

BY BRUNO WOJCIK AND HOMER ADKINS

Three brief references have appeared with respect to the catalytic hydrogenation of amides to amines. Mailhe[1] in a brief note reported the formation of ethyl and diethyl amines from acetamide and of propyl and dipropylamines from propionamide in the vapor phase ($Ni + H_2$), but no details as to yields or purity of products were given. Attempts to confirm Mailhe's results in this Laboratory by Mr. Frank Signaigo have failed to produce amines from acetamide in yields greater than 1%. In this Laboratory N-*n*-caproylpiperidine has been converted in good yield to N-*n*-hexylpiperidine over copper–chromium oxide,[2] while more recently a method has been described which apparently may be used quite generally for the hydrogenation of amides.[3] This latter process, which involves the reaction of an amide with hydrogen over copper–chromium oxide in a diluent for water such as dioxane, has now been applied to various types of amides.

It may clarify the experimental results summarized in Table I if the types of reaction which occur in the hydrogenation of amides over copper–chromium oxide are outlined. First the hydrogenolysis of the oxygen of an amide may result in the formation of a primary, secondary or tertiary amine depending upon whether or not the amide carries substituents upon the nitrogen.

$$RC(O)NH_2 \xrightarrow{H_2} RCH_2NH_2 + H_2O \qquad \text{Ia}$$

$$RC(O)NHR' \xrightarrow{H_2} RCH_2NHR' + H_2O \qquad \text{Ib}$$

$$RC(O)NR_2' \xrightarrow{H_2} RCH_2NR_2' + H_2O \qquad \text{Ic}$$

In mono- and especially in di-substituted amides there occurred a cleavage of nitrogen to carbon bonds.

$$RC(O)NHR' \xrightarrow{H_2} RCH_2NH_2 + R'H + H_2O \qquad \text{IIa}$$

$$\xrightarrow{H_2} RCH_3 + R'NH_2 + H_2O \qquad \text{IIb}$$

$$RC(O)NR_2' \xrightarrow{H_2} RCH_2NHR' + R'H + H_2O \qquad \text{IIa}'$$

$$\xrightarrow{H_2} RCH_3 + R_2'NH + H_2O \qquad \text{IIb}'$$

The cleavage may occur at the nitrogen rather than at the oxygen linkage with the formation of an alcohol. This reaction has taken place almost exclusively in attempts to reduce amides in an aqueous or alcoholic medium.[4]

$$RC(O)NH_2 \xrightarrow{H_2} RCH_2OH + NH_3 \qquad \text{III}$$

In addition to these three primary types of reaction certain secondary reactions occur, among which the formation of secondary from primary amines is by far the most important.

$$RNH_2 + RNH_2 \longrightarrow R_2NH + NH_3 \qquad \text{IV}$$

The water, ammonia or amines produced as above may bring about the hydrolysis, ammonolysis or aminolysis of the amide, and also any alcohol produced may alkylate an amine.

$$RC(O)NH_2 + H_2O \longrightarrow RCOOH + NH_3 \qquad \text{V}$$

$$RC(O)NHR + NH_3 \longrightarrow RC(O)NH_2 + RNH_2 \qquad \text{VI}$$

$$RC(O)NH_2 + RNH_2 \longrightarrow RC(O)NHR + NH_3 \qquad \text{VII}$$

$$ROH + R'NH_2 \longrightarrow RNHR' + H_2O \qquad \text{VIII}$$

Reactions I, II and III are established by the experimental results reported in this paper. Reactions IV and VIII have been observed by a number of investigators,[5] while reactions V, VI and VII are common types.

Preliminary experiments showed that in general it was impractical to hydrogenate an amide unless some diluent for water was used as a reaction medium. Otherwise reaction V took place and the acid and ammonia so formed deactivated the catalyst. When ethanol was used as a solvent the hydrogenation proceeded rapidly but the product was an alcohol rather than an

---

(1) Mailhe, *Bull. soc. chim.*, (3) **35**, 614 (1906).

(2) Folkers and Adkins, THIS JOURNAL, **54**, 1152 (1932).

(3) Adkins and Wojcik, *ibid.*, **56**, 247 (1934).

(4) *Cf.* Scheuble and Loebl, *Monatsh.*, **25**, 341 (1904).

(5) For references see Winans and Adkins, THIS JOURNAL, **55**, 4167 (1933).