

THE CONSTITUENTS OF DERRIS AND OTHER ROTENONE-BEARING PLANTS

H. L. HALLER, L. D. GOODHUE, AND HOWARD A. JONES

*Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture,
Washington, D. C.*

Received October 1, 1941

I. INTRODUCTION

The wide interest in *Derris*, *Lonchocarpus*, *Tephrosia*, *Mundulea*, and other rotenone-bearing plants is attested by the many articles (64) relating to them that have appeared in the literature during the past fifteen years. The roots of these plants, all closely related botanically and belonging to the family *Fabaceae*, are used in large quantities for the preparation of dusts and sprays for combating many injurious insects.

More than six and a half million pounds of *Derris* and *Lonchocarpus*,¹ the most important genera commercially, were imported into the United States in 1940. The former is obtained from British Malaya and the Dutch East Indies and the latter from South America.

The rotenone-bearing plants have been shown to be toxic to many widely different species of insects (65). McIndoo, Sievers, and Abbott (57), in an extensive study of derris as an insecticide, have demonstrated that it acts both as a contact insecticide and as a stomach poison. Tischler's studies (77) on the physiological mode of toxicity of derris to insects have been summarized by Holman (40) as follows:

"... (1) that extracts enter the insect's body by (a) the alimentary canal, through (b) spiracles and tracheal system, and (c) through the integument, and that there is for certain insects a definite stomach-poisoning effect; (2) that dusts penetrate by (a) and (c), but probably not by (b); (3) that body exudates and body fluids may extract the poison, that there are thin surface areas through which osmosis can take place, and that derris dust settling on these (areas containing body exudates) finds continuous access to the body until death takes place; (4) that there are no specific effects on motor nerves and attached muscles, and that circulation effects are secondary in character; (5) that derris acts primarily by the inhibition of oxygen utilization, and that this effect is general rather than specific to any organ or system."

Derris and allied materials in large doses exercise some toxic action upon man and higher animals, but they are far less toxic than the arsenicals which are used for insecticidal purposes. Haag (32) considered that there was little danger of acute poisoning to healthy subjects following the ingestion of derris on foods, but workers in derris dusts should be protected by respirators.

The insecticidal action of the roots was attributed at first to a single constituent, rotenone (52, 62). This compound separates in optically active, crystalline

¹ Commonly called cube, barbasco, haiari, timbo, and nekoe. These names, however, are not only applied to *Lonchocarpus* but are used for other entirely unrelated fish-poison plants, many of which are of no insecticidal value.

form when extracts of the roots, made with suitable organic solvents, are concentrated. The extracts contain a number of related compounds other than rotenone, which are obtained as an uncrystallizable residue after complete evaporation of the solvent. The percentage of total extractives, as well as the proportion of rotenone to total extractives, varies widely and depends upon several factors, such as the species, the method of cultivation, and the solvent used in the extraction. In the case of derris, which has been most extensively studied, the residue, when freed from rotenone as completely as possible, is known as derris resin.² The resins, like rotenone, are usually optically active and most of them are levorotatory.

In 1930 Clark (14) found that derris resin, on treatment with alkali, yielded several crystalline optically inactive substances, which he named deguelin, tephrosin, and toxicarol. Tests on all three compounds against aphids by Davidson (23), against silkworms by Shepard and Campbell (68), and against mosquito larvae by Campbell and Sullivan (unpublished data) indicated that deguelin was much less toxic than rotenone, while tephrosin and toxicarol were practically non-toxic. From these results the erroneous conclusion was drawn that the extractives other than rotenone had little or no insecticidal value, and the toxicity of the derris resin was ascribed to its occluded rotenone. Various comparative tests of derris extractives and rotenone, however, have indicated that toxic substances other than rotenone must be present in the extractives. For example, Jones *et al.* (44) found that powdered derris extractives that contained about 25 per cent of rotenone were as toxic to mosquito larvae as was pure rotenone, and Campbell *et al.* (13) found that a kerosene extract of derris from which no rotenone could be isolated was effective against houseflies. These results, as well as those of Tattersfield and Martin (56, 73), have led to further intensive investigations of derris resin from a number of species and varieties of *Derris* root. Studies have also been made on other rotenone-bearing legumes, of which the most important are species of *Tephrosia* and *Lonchocarpus*.

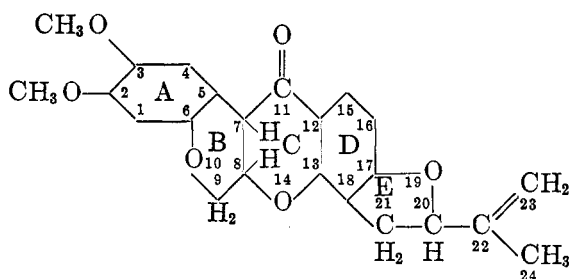
The isolation of rotenone by Clark (21) from the roots of *Tephrosia virginiana* L., the most abundant species of *Tephrosia* indigenous to the United States, stimulated interest in this plant as a source of insecticides. Analytical studies (43) of samples of this plant, commonly known as devil's shoestring, have shown considerable variation in the amount of insecticidal constituents, but recent selective breeding experiments (55, 69) make it now possible to produce a root of uniformly high quality. Limited quantities of these new varieties have been available for studies on their chemical constituents (29).

II. CHEMISTRY OF ROTENONE AND RELATED COMPOUNDS

A. Rotenone

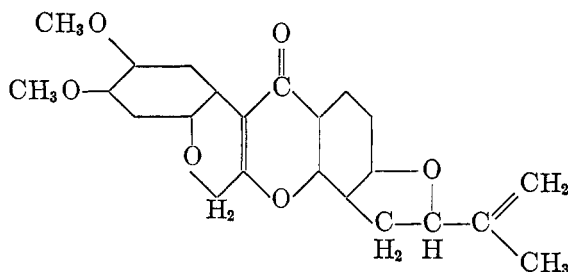
Through the efforts of three groups of chemists the structural formula for rotenone is now unreservedly accepted to be I, and for an understanding of the fundamentals of its chemistry the reader is referred to reviews by LaForge, Haller, and Smith (50), Butenandt and McCartney (8), and King (48).

² The term "deguelin concentrate" has also been used, but we regard this term as less appropriate.



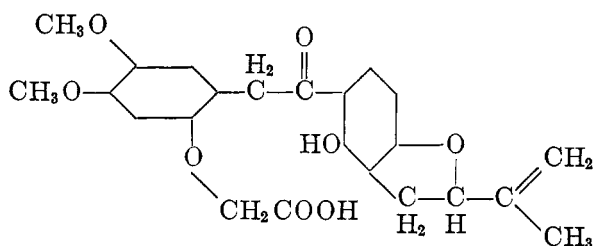
I
Rotenone

One of the reactions of rotenone, common to most of the compounds isolated from the uncrystallizable fraction of the extractives, is the loss of two hydrogen atoms on gentle oxidation, with the formation of dehydrorotenone (II) (6). On

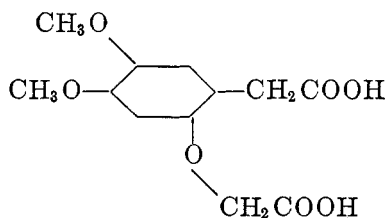


II
Dehydrorotenone

treatment with alcoholic potash this compound adds two molecules of water to form derrisic acid (III) (53), which when oxidized with hydrogen peroxide yields derric acid (IV). With potassium permanganate derric acid yields a

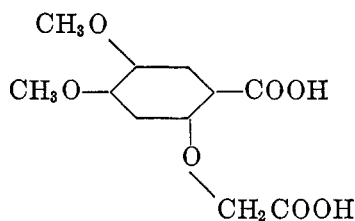


III
Derrisic acid

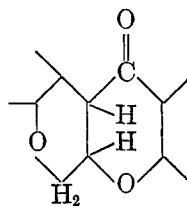


IV
Derric acid

lower homolog, risic acid (V) (54). This sequence of reaction is shown by all the compounds having a chromane-chromanone ring system (VI).



V
Risic acid

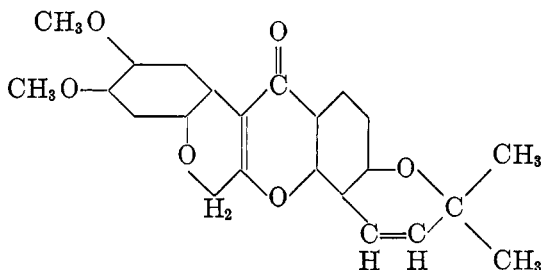


VI
Chromane-chromanone
system

B. Deguelin

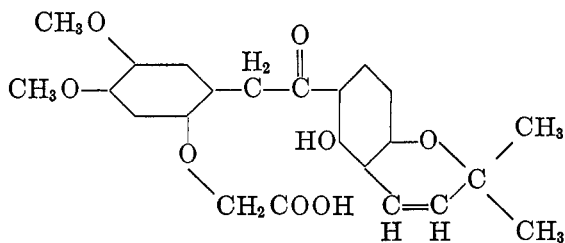
Deguelin was first described by Clark (16), who obtained it in optically inactive crystalline form on treatment of an alcoholic solution of derris resin with alkali.³ It has also been obtained from cube, *Tephrosia*, etc.

Deguelin has the molecular formula $C_{23}H_{22}O_6$, and is thus isomeric with rotenone. Like the latter it possesses two methoxyl groups and with mild oxidizing agents yields the dehydro compound, dehydrodeguelin (VII) (16), which on treatment with alcoholic alkali adds two molecules of water with the formation



VII
Dehydrodeguelin

of deguelic acid (VIII). Oxidation of this compound in alkaline solution with

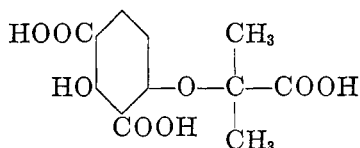


VIII
Deguelic acid

³ The isodeguelin obtained by Merz (58) from the seeds of *Cracca vogelii* has been shown by Boam, Cahn, and Stuart (3) to be identical with deguelin.

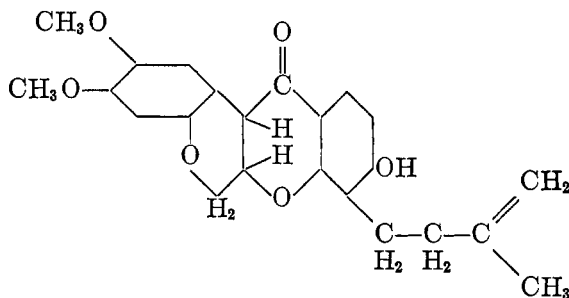
hydrogen peroxide yields derric acid (IV). It thus follows that in deguelin, as in rotenone, derric acid is derived from one half of the molecule, and hence the structural differences between deguelin and rotenone are to be found in the second half of the molecule or in the linkages between the two parts.

Oxidation of dehydrodeguelin with potassium permanganate yields, besides 2-hydroxy-4,5-dimethoxybenzoic acid and risic acid, nicouic acid (18). Nicouic acid is a tricarboxylic acid having the structure represented by formula IX.



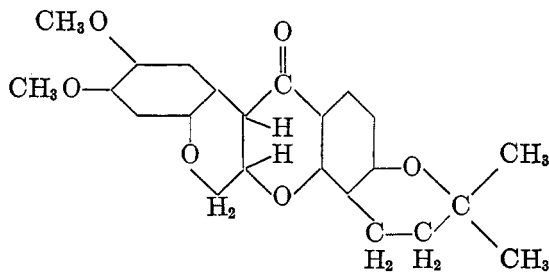
IX
Nicouic acid

The absence of methoxyl groups shows it to be derived from the undetermined half of the deguelin molecule. The isolation of this acid, together with the fact that rotenonic acid (isodihydrorotenone) (X), which is obtained on catalytic hydrogenation of rotenone, is isomerized with sulfuric acid to β -dihydrorotenone



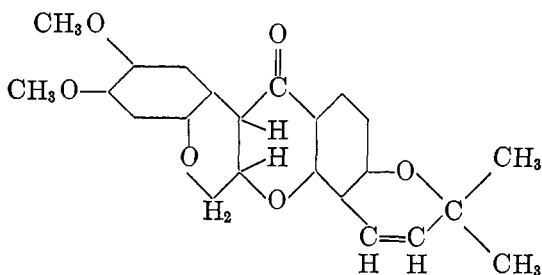
X
Rotenonic acid

(XI) (33), the optically inactive form of which is identical with dihydrodeguelin,



XI
 β -Dihydrorotenone (dihydrodeguelin)

showed deguelin to possess the structural formula XII. This structure differs

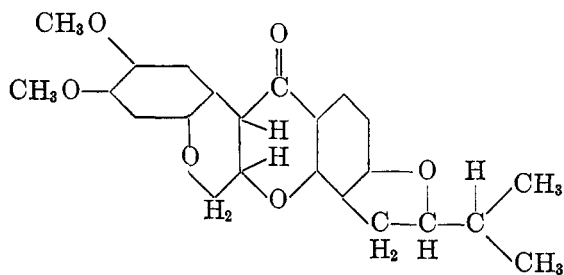


XII

Deguelin

from that of rotenone in that ring E is a substituted chromene, whereas in rotenone it is a substituted dihydrofuran. Also rotenone possesses three asymmetric carbon atoms, numbers 7, 8, and 20, while deguelin has but two, numbers 7 and 8. Carbon atoms 7 and 8 may be regarded as one asymmetric center and carbon atom 20 as another. The effect of alkali on these centers has recently been studied by Cahn *et al.* (11). Like rotenone (41, 45) deguelin crystallizes from certain organic liquids with a definite molecular ratio of solvent of crystallization (27). Gravimetric methods for the determination of deguelin have been proposed by Takei *et al.* (71) and by Goodhue and Haller (28).

The relatively low insecticidal action of deguelin (23, 68) stimulated studies on its precursor. Haller and LaForge (34) found that, on hydrogenation of derris resin in the absence of alkali, optically active dihydrodeguelin (β -dihydrorotenone) was obtained. This compound possesses an insecticidal value of the same order as dihydrorotenone (XIII) and rotenone (25, 70). The type of hydrogenation



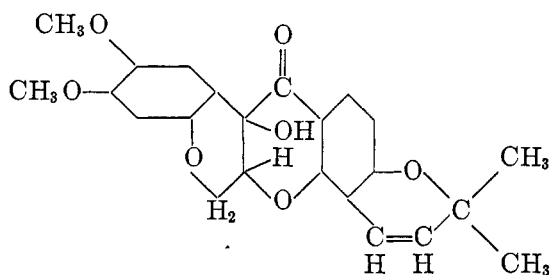
XIII

Dihydrorotenone

tion procedure used made it appear probable that at least part of the deguelin was present in the resin in an optically active form. The conclusions of Haller and LaForge have since received support by the work of Tattersfield and Martin (74), Cahn and his collaborators (12), and Harper (36).

C. Tephrosin

Hanriot (35) in 1907 isolated from the leaves of *Tephrosia vogelii* a substance which he named tephrosin. Similar results were obtained in 1915 by an anonymous worker (1), and in 1926 Tattersfield *et al.* (72) obtained two apparently different substances⁴ having higher melting points than Hanriot's product. Clark (17) obtained a crystalline material corresponding to that described by Hanriot from the same source and showed it to be a mixture of two compounds. One was deguelin and the other a colorless crystalline substance that Clark designated tephrosin. Clark also isolated this compound from the mixture of crystalline substances obtained on treatment of derris resin in alcohol with alkali. He showed that it had the molecular formula $C_{23}H_{22}O_7$, was optically inactive, and possessed two methoxyl groups. On treatment with acetic anhydride or acetic and sulfuric acids, tephrosin loses a molecule of water and dehydrodeguelin (VII) is formed. It is thus clear that tephrosin (XIV) is a hydroxydeguelin. Since it has been shown that dehydrodeguelin results from deguelin by the loss



XIV
Tephrosin

of hydrogen atoms from carbon atoms 7 and 8, it follows that tephrosin possesses a hydroxyl group in place of a hydrogen atom on one of these two carbon atoms. No information is available, however, as to the exact configuration of tephrosin.

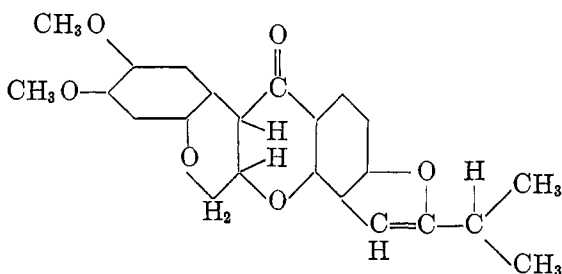
An isomer of tephrosin, isotephrosin, has been isolated from a Peruvian cube root (22). With dehydrating agents it also yields dehydrodeguelin. Isotephrosin therefore is also a hydroxydeguelin and has the same relation to deguelin as has tephrosin. If the hydroxyl group of the latter is on carbon atom 7, then in isotephrosin it would be on carbon atom 8, or *vice versa*.

A third isomer of tephrosin, designated hydroxydeguelin-C (49), has also been described. It was prepared from deguelin by oxidation with hydrogen peroxide in alcoholic alkaline solution. It differs from tephrosin especially in its behavior toward dehydrating agents, for it was recovered unchanged after several hours' boiling with 8 per cent alcoholic sulfuric acid.

By the method of oxidation described above, isorotenone (XV), which is obtained on treatment of rotenone with mineral acid, yields two hydroxy com-

⁴ Several years ago it was shown that one of the compounds was probably slightly impure tephrosin and the other a pure sample of tephrosin.

pounds, designated isorotenone-C and isorotenone-D, both of which are stable to dehydrating agents.



XV
Isorotenone

The two normal hydroxyisorotenones corresponding to tephrosin and iso-tephrosin have also been prepared. Both are readily dehydrated to the same dehydro compound (dehydroisorotenone). LaForge and Haller (49) have suggested that these isomers may be accounted for on the basis of spatial configuration, but this explanation has not met with ready acceptance.

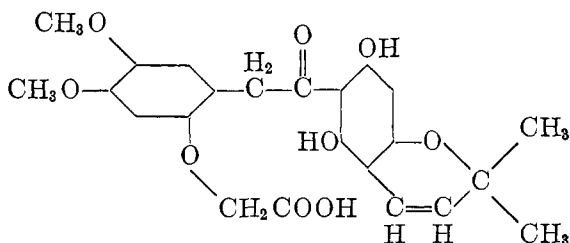
In 1933 Takei *et al.* (71) produced evidence that tephrosin does not occur as such in derris but is formed by oxidation of deguelin. These findings were supplemented by those of LaForge and Haller (49) that deguelin in alkaline solution is readily oxidized by air to a mixture of tephrosins, and those of Merz and Schmidt (59) that when a chloroform solution of deguelin is shaken with aqueous alkali it is partly oxidized to tephrosin. Cahn, Phipers, and Boam (12) also produced evidence that tephrosin is an oxidation product, and now all workers in this field seem agreed that tephrosin does not occur naturally in the resin. The allotephrosin and isoallotephrosin of Merz and Schmidt (59) have been shown to be identical with tephrosin (3).

D. Toxicarol

Clark (15) was the first to describe toxicarol. He obtained it in optically inactive form by alkali treatment of the extractives of the roots of *Tephrosia toxicaria* and from derris resin. Subsequently Cahn and Boam (9) showed that extracts of a certain species of derris giving no rotenone (63) by the usual carbon tetrachloride method nearly always yielded pure toxicarol on treatment with alkali. Because of its origin they have chosen to designate this kind of derris as being of the "Sumatra type." Such root has been referred to by Buckley (5) and by Harper (38) as "Kinta type" derris, because their specimens came from the Kinta district of Malaya.

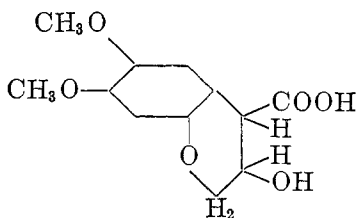
Toxicarol has the molecular formula $C_{23}H_{22}O_7$ (7, 15), being isomeric with tephrosin but, unlike it, possesses a phenolic hydroxyl group. Like rotenone it yields a dehydro compound (19) that adds two molecules of water with the formation of toxicarolic acid (XVI), and this in turn can be degraded to derric acid.

Thus it is shown that toxicarol possesses a chromane-chromanone nucleus of the rotenone type.

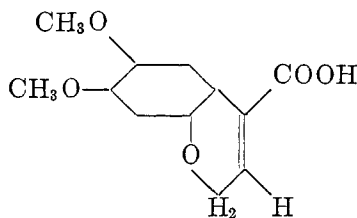


XVI
Toxicarolic acid

On treatment with alkali toxicarol loses C_5H_6 , yielding apotoxicarol (20); this reaction is not shown by rotenone or deguelin. Apotoxicarol on oxidation in alkaline solution yields two monocarboxylic acids, hydroxyneticoric acid

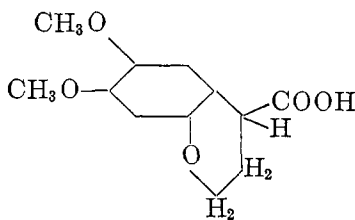


XVII
Hydroxyneticoric acid

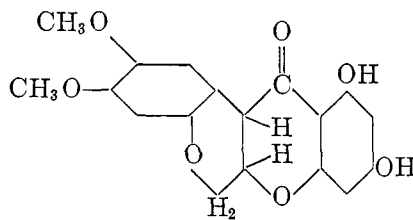


XVIII
Dehydroneticoric acid

(XVII) and dehydroneticoric acid (XVIII). The former may be dehydrated to the latter, which on hydrogenation is reduced to netoric acid (XIX). Apotoxi-



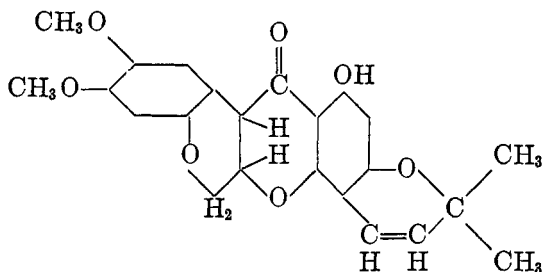
XIX
Netoric acid



XX
Apotoxicarol

carol undergoes the reactions characteristic of the chromane-chromanone residue and has been assigned formula XX. This structure has received confirmation by the synthesis of apotoxicarolic acid, which is formed on hydrolysis of dehydroapotoxicarol. Toxicarol and deguelin yield acetone on treatment with alkali under the proper conditions. This reaction indicates the grouping $(CH_3)_2C$ and supports the theory that toxicarol also contains the 2,2-dimethyl- Δ^3 -

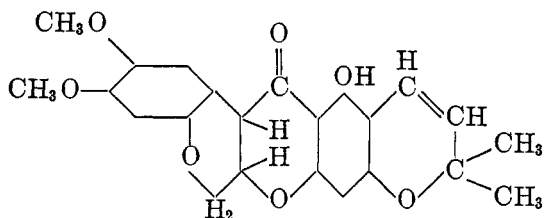
chromene residue characteristic of deguelin. On the basis of this evidence and by analogy, toxicarol has been tentatively assigned the formula XXI (26).



XXI
 α -Toxicarol

Substantiation of the nature of the chromene system just postulated was furnished by Bridge *et al.* (4). Their evidence has recently been summarized by LaForge and Markwood (51).

When optically inactive toxicarol in acetone solution is heated with potassium carbonate, it is partly changed to an isomer, β -toxicarol (XXII) (11), the linear



XXII
 β -Toxicarol

form of formula XXI. Its greater solubility in ether permits a separation of β -toxicarol from ordinary toxicarol (XXI), designated α -toxicarol. The reaction is reversible, but when alcoholic alkali is used the much less soluble α -form crystallizes out, so that in alcohol the change from the β -form to the α -form is almost complete. Usually, however, the α -form contains a small amount of the β -form, and this largely accounts for the various melting points reported for ordinary toxicarol: 213°C. by Butenandt and Hilgetag (7), 219°C. (corr.) by Clark (15), and 232–233°C. by Cahn, Phipers, and Boam (11), who have devised a method for purifying the α -form. Jones and Wood (46) have recently found that in capillary melting-point tubes made of soft-glass tubing the melting point of toxicarol is appreciably lower than in hard glass or Pyrex capillary tubes. The phenomenon has been shown to be due to the greater alkalinity of the soft-glass tubing.

Toxicarol that is obtained by the action of alkali on derris extractives is optically inactive. That it does not occur in this form in the root was first demonstrated by Tattersfield and Martin (75, 76). They succeeded in isolating from

a Sumatra-type derris resin an optically active precursor, which was shown by Cahn *et al.* (11) to be *l*- α -toxicarol. The latter workers doubted the purity of Tattersfield's preparation, but Harper (38) has concluded that the optical data of Cahn *et al.* are untrustworthy and that their criticism of the work of Tattersfield and Martin is unjustified. The properties of the protoxicarol of Rowaan and Van Duuren (67), levorotatory in benzene and dextrorotatory in acetone, indicate it to be *l*- α -toxicarol.

Tattersfield and Martin (76) have shown the toxicarol precursor to be about one-fifteenth as toxic as rotenone to *Aphis rumicis* L. The Sumatra-type derris resin from which it was isolated was about one-sixth as toxic as rotenone or about half as toxic as samples of *Derris elliptica* resin.

E. Sumatrol

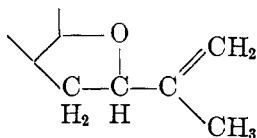
Sumatrol was first isolated by Cahn and Boam (10) from a Sumatra-type derris resin,⁵ from which it was subsequently also obtained by other workers. It has not yet been found in *Derris elliptica*. While, according to Tattersfield and Martin (76), sumatrol is about as toxic as toxicarol to *Aphis rumicis*, it is present in the resin only in small amount and therefore is not regarded as an important contribution to the insecticidal effect of the resin.

Sumatrol is optically active and has the molecular formula $C_{23}H_{22}O_7$ (10), being isomeric with tephrosin and toxicarol. It differs from tephrosin in being phenolic and from toxicarol in being colorless.

Besides having a phenolic hydroxyl group, sumatrol, like all other members of the rotenone series, possesses two methoxyl groups, an active carbonyl group, and three chemically inactive oxygen atoms (66). Further, it yields a dehydro compound which furnishes an acid of the derrisic type by standard procedures. It therefore appears practically certain that sumatrol possesses the chromane-chromanone ring system which makes the chromene-chromone system capable of forming the derrisic acid type of compound.

The similarity of the colors given with ferric chloride and the insolubility in aqueous alkali suggested that sumatrol, like toxicarol, has a hydroxyl group in the 5-position of ring D.

On hydrogenation sumatrol, like rotenone, yields a dihydro compound and a tetrahydro derivative. Both compounds are optically active and both form dehydro derivatives, but only the dihydrodehydro compound rotates the plane of polarized light. These facts are strong evidence that sumatrol, like rotenone,

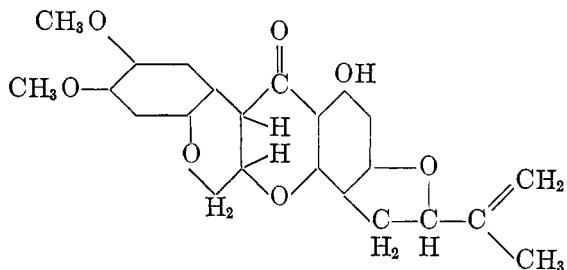


XXIII

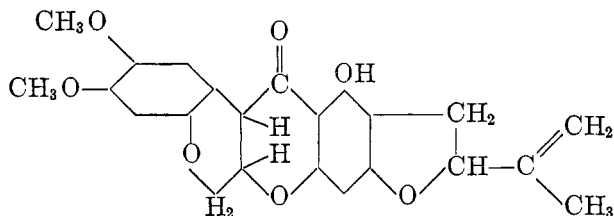
Isopropenyldihydrofuran system

⁵ The root was probably *Derris malaccensis* var. *sarawakensis*.

contains the system XXIII. Consequently it would appear that sumatrol is a hydroxyrotenone and may be represented by formula XXIV. The less likely linear formula XXV has also been considered (66).



XXIV
Sumatrol



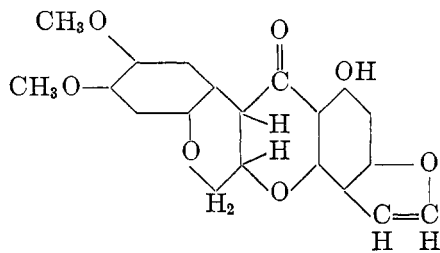
XXV
Sumatrol (linear formula)

The synthesis of tetrahydrosumatrollic acid and of dehydrotetrahydrosumatrol (47) substantiates the presence of the chromane-chromanone system in sumatrol and also makes certain the presence of the hydroxyl group in the 5-position of ring D, but it does not permit a final choice between formulas XXIV and XXV.

F. Malaccol

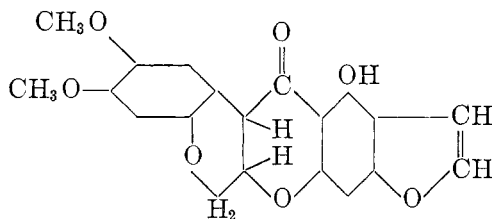
From the concentrated ether extract of a sample of Sumatra-type derris containing no rotenone and 23.7 per cent of total extractives, Meyer and Koolhaas (60) obtained a small amount of a yellowish solid material. On purification this material yielded greenish yellow needle-shaped crystals, which were optically active. The same compound was also obtained a short time later by Harper (39) from the same type of derris.

From its analysis, which indicates the molecular formula $C_{20}H_{16}O_7$, and from the fact that, like toxicarol, it gives a green color with alcoholic ferric chloride, Meyer and Koolhaas (60) proposed the structural formula XXVI for malaccol.



XXVI
Malaccol

After a detailed study of the compound Harper (39) independently proposed the same formula. He found that malaccol gives a positive Durham test, and has two methoxyl groups and an active carbonyl group, as shown by the formation of an oxime. These facts indicate that rings A, B, and C are the same as in rotenone. The strong ferric chloride reaction indicates that there is a phenolic hydroxyl group in the position ortho to the carbonyl group. In agreement with this conclusion it has been observed that malaccol, like sumatrol, is almost insoluble in aqueous alkali. That ring D is a phloroglucinol residue is shown by the close similarity of the ferric chloride colors given by malaccol and its dihydro and tetrahydro derivatives to those of the corresponding derivatives of sumatrol, in which the presence of a phloroglucinol residue has recently been confirmed by synthesis. Harper (39) points out, however, that the experimental data do not distinguish between the angular formula (XXVI) and the less likely linear formula (XXVII). Formula XXVI bears the same structural relation to elliptone as do sumatrol to rotenone and toxicarol to deguelin.



XXVII

Malaccol (linear formula)

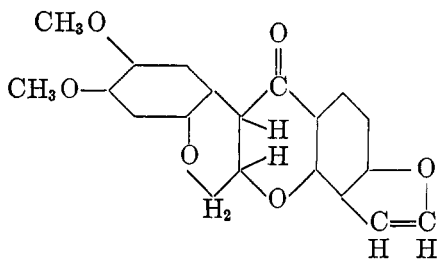
G. *Elliptone*

Several years ago Buckley (5) found that an ethereal solution of *Derris elliptica* resin that had been repeatedly treated with 5 per cent potassium hydroxide solution deposited crystals on standing. The purified compound, called at first Buckley's compound and subsequently elliptone⁶ (37), was optically inactive, and the suggestion was therefore made that the compound probably did not occur in the resin as such. This surmise proved correct, for a short time later (36, 37, 60) an optically active isomer that could be racemized to *dl*-elliptone was obtained. Both compounds yielded the same dehydro compound, thus confirming further their relationship. The speculation of Boam and Cahn (2) that elliptone is a degradation product of deguelin was therefore untenable. Preliminary insecticidal tests (61) indicate that elliptone is comparable with rotenone in its toxicity to caterpillars.

The molecular formula $C_{20}H_{16}O_6$ (36, 37, 60) was established for elliptone. It shows color tests characteristic of rotenone and closely related compounds, forms an oxime and a dehydro compound, and gives the degradation products obtainable from related compounds having a chromane-chromanone ring system. Although the evidence presented makes the proposed structural formula XXVIII

⁶ The term "derride" proposed for this substance has already been used by Greshoff (31) for a resinous extract from *Derris elliptica* root.

probable, final proof can be afforded only by degradation to compounds of known structure or by synthesis.



XXVIII
Elliptone

H. Other constituents

By steam distillation of an extract of the leaves of *Tephrosia vogelii*, Hanriot (35) isolated an oily liquid of the formula $C_{10}H_{16}O$. The compound had the reducing properties of an aldehyde, but no definite derivatives could be prepared. The non-crystalline part of the extractives from *T. virginiana* was investigated

TABLE 1
Relative toxicity to insects of rotenone and allied substances

SUBSTANCE	APPROXIMATE RELATIVE TOXICITY	TEST INSECT	REFERENCE
Rotenone.....	100		
Deguelin (inactive).....	10	Bean aphid (<i>Aphis rumicis</i> L.)	(23)
	10	Housefly (<i>Musca domestica</i> L.)	(70)
	30	Silkworm (<i>Bombyx mori</i> L.)	(68)
Deguelin concentrate (active)...	50	Housefly (<i>Musca domestica</i> L.)	(70)
Tephrosin (inactive).....	2	Bean aphid (<i>Aphis rumicis</i> L.)	(23)
	10	Silkworm (<i>Bombyx mori</i> L.)	(68)
Toxicarol (inactive).....	<1	Bean aphid (<i>Aphis rumicis</i> L.)	(23)
Toxicarol (active).....	7	Bean aphid (<i>Aphis rumicis</i> L.)	(76)
Sumatrol (active).....	7	Bean aphid (<i>Aphis rumicis</i> L.)	(76)
	70	Housefly (<i>Musca domestica</i> L.)	(70)
Dihydrorotenone (active).....	>30	Silkworm (<i>Bombyx mori</i> L.)	(68)
Dihydrodeguelin (inactive).....	<3	Housefly (<i>Musca domestica</i> L.)	(70)
Dihydrodeguelin (active).....	50	Housefly (<i>Musca domestica</i> L.)	(70)
Dehydrorotenone (active).....	0	Imported cabbage worm (<i>Asciarapae</i> (L.))	(24)

by Goodhue and Haller (29), and was found to contain a considerable amount of an oil composed mostly of sesquiterpenes. Two crystalline compounds were isolated by a process including adsorption on charcoal and molecular distillation. One of these, melting at 131°C . and having the molecular formula $C_{21}H_{22}O_4$, had previously been isolated by Clark (21). The other was an orange-yellow crystalline compound melting at 125°C . Analyses indicate the molecular formula to be $C_{22}H_{24}O_4$. Neither of these compounds showed any toxicity to houseflies (30).

A crystalline material of an acidic nature has been isolated from an unknown species of *Lonchocarpus* by Jones (42). The substance, melting at 201°C. but probably dimorphic, was called lonchocarpic acid. It had the molecular formula $C_{26}H_{26}O_6$ with one methoxy group.

III. TOXICITY TO INSECTS OF ROTENONE AND RELATED COMPOUNDS

Many toxicity tests have been made of the compounds discussed in this paper. In table 1 a brief summation is given of the approximate relative toxicities, on the basis of rotenone as 100, of some constituents of derris and cube and their derivatives. All substances can be compared with rotenone, but direct comparison of the compounds with each other is not entirely valid, as all were not tested in the same way or against the same insect. Comparisons are further complicated by the use of different criteria for toxicity.

REFERENCES

- (1) ANONYMOUS: Bull. Imp. Inst. **13**, 61 (1915).
- (2) BOAM, J. J., AND CAHN, R. S.: J. Chem. Soc. **1938**, 1818.
- (3) BOAM, J. J., CAHN, R. S., AND STUART, A.: J. Soc. Chem. Ind. **56**, 91T (1937).
- (4) BRIDGE, W., HEYES, R. G., AND ROBERTSON, A.: J. Chem. Soc. **1937**, 279.
- (5) BUCKLEY, T. A.: J. Soc. Chem. Ind. **55**, 285T (1936); Chemistry & Industry **57**, (45), 1059 (1938).
- (6) BUTENANDT, A.: Ann. **464**, 253 (1928).
- (7) BUTENANDT, A., AND HILGETAG, G.: Ann. **495**, 172 (1932); **506**, 158 (1933).
- (8) BUTENANDT, A., AND MCCARTNEY, W.: Ann. **494**, 17 (1932).
- (9) CAHN, R. S., AND BOAM, J. J.: J. Soc. Chem. Ind. **54**, 37T (1935).
- (10) CAHN, R. S., AND BOAM, J. J.: J. Soc. Chem. Ind. **54**, 42T (1935).
- (11) CAHN, R. S., PHIPERS, R. F., AND BOAM, J. J.: J. Chem. Soc. **1938**, 513, 734.
- (12) CAHN, R. S., PHIPERS, R. F., AND BOAM, J. J.: J. Soc. Chem. Ind. **57**, 200 (1938).
- (13) CAMPBELL, F. L., SULLIVAN, W. N., AND JONES, H. A.: Soap **10** (3), 81 (1934).
- (14) CLARK, E. P.: Science **71**, 396 (1930).
- (15) CLARK, E. P.: J. Am. Chem. Soc. **52**, 2461 (1930).
- (16) CLARK, E. P.: J. Am. Chem. Soc. **53**, 313 (1931).
- (17) CLARK, E. P.: J. Am. Chem. Soc. **53**, 729 (1931).
- (18) CLARK, E. P.: J. Am. Chem. Soc. **53**, 2007 (1931); **54**, 3000 (1932).
- (19) CLARK, E. P.: J. Am. Chem. Soc. **53**, 2264 (1931).
- (20) CLARK, E. P.: J. Am. Chem. Soc. **54**, 2537 (1932).
- (21) CLARK, E. P.: Science **77**, 311 (1933).
- (22) CLARK, E. P., AND CLABORN, H. V.: J. Am. Chem. Soc. **54**, 4454 (1932).
- (23) DAVIDSON, W. M.: J. Econ. Entomol. **23**, 877 (1930).
- (24) DAVIDSON, W. M., AND JONES, H. A.: J. Econ. Entomol. **24**, 257 (1931).
- (25) FINK, D. E., AND HALLER, H. L.: J. Econ. Entomol. **29**, 594 (1936).
- (26) GEORGE, S. W., ROBERTSON, A., SUBRAMANIAM, T. S., AND HILTON, W.: J. Chem. Soc. **1937**, 1535.
- (27) GOODHUE, L. D., AND HALLER, H. L.: J. Am. Chem. Soc. **61**, 486 (1939).
- (28) GOODHUE, L. D., AND HALLER, H. L.: Ind. Eng. Chem., Anal. Ed. **11**, 640 (1939).
- (29) GOODHUE, L. D., AND HALLER, H. L.: J. Am. Chem. Soc. **62**, 2520 (1940).
- (30) GOODHUE, L. D., AND SULLIVAN, W. N.: J. Econ. Entomol. **34**, 77 (1941).
- (31) GRESHOFF, M.: Ber. **23**, 3538 (1890).
- (32) HAAG, H. B.: J. Pharmacol. **43**, 193 (1931).
- (33) HALLER, H. L.: J. Am. Chem. Soc. **54**, 2126 (1932).
- (34) HALLER, H. L., AND LaFORGE, F. B.: J. Am. Chem. Soc. **56**, 2415 (1934).
- (35) HANBIOT, M.: Compt. rend. **144**, 150, 190 (1907).

- (36) HARPER, S. H.: J. Chem. Soc. **1939**, 1099.
(37) HARPER, S. H.: Chemistry & Industry **58**, 292 (1939).
(38) HARPER, S. H.: J. Chem. Soc. **1939**, 812.
(39) HARPER, S. H.: J. Chem. Soc. **1940**, 309.
(40) HOLMAN, H. J.: *A Survey of Insecticide Materials of Vegetable Origin*, p. 50. Imperial Institute, London (1940).
(41) JONES, H. A.: J. Am. Chem. Soc. **53**, 2738 (1931).
(42) JONES, H. A.: J. Am. Chem. Soc. **56**, 1247 (1934).
(43) JONES, H. A., CAMPBELL, F. L., AND SULLIVAN, W. N.: Soap **11** (9), 99 (1935).
(44) JONES, H. A., GERSDORFF, W. A., GOODEN, E. L., CAMPBELL, F. L., AND SULLIVAN, W. N.: J. Econ. Entomol. **26**, 451 (1933).
(45) JONES, H. A., AND SMITH, C. M.: J. Am. Chem. Soc. **52**, 2554 (1930).
(46) JONES, H. A., AND WOOD, J. W.: J. Am. Chem. Soc. **63**, 1760 (1941).
(47) KENNY, T. S., ROBERTSON, A., AND GEORGE, S. W.: J. Chem. Soc. **1939**, 1601.
(48) KING, H.: Annual Reports of the Chemical Society **29**, 186 (1932).
(49) LAFORGE, F. B., AND HALLER, H. L.: J. Am. Chem. Soc. **56**, 1620 (1934).
(50) LAFORGE, F. B., HALLER, H. L., AND SMITH, L. E.: Chem. Rev. **12**, 182 (1933).
(51) LAFORGE, F. B., AND MARKWOOD, L. N.: Ann. Rev. Biochem. **7**, 473 (1938).
(52) LAFORGE, F. B., AND SMITH, L. E.: J. Am. Chem. Soc. **51**, 2574 (1929).
(53) LAFORGE, F. B., AND SMITH, L. E.: J. Am. Chem. Soc. **52**, 1091 (1930).
(54) LAFORGE, F. B., AND SMITH, L. E.: J. Am. Chem. Soc. **52**, 2878 (1930).
(55) LITTLE, V. A.: J. Econ. Entomol. **24**, 743 (1931); **23**, 707 (1935).
(56) MARTIN, J. T.: Ann. Applied Biol. **27**, 274 (1940).
(57) MCINDOO, N. E., SIEVERS, A. F., AND ABBOTT, W. S.: J. Agr. Research **17**, 177 (1919).
(58) MERZ, K. W.: Arch. Pharm. **270**, 362 (1932).
(59) MERZ, K. W., AND SCHMIDT, G.: Arch. Pharm. **273**, 1 (1935).
(60) MEYER, T. M., AND KOOLHAAS, D. R.: Rec. trav. chim. **58**, 207 (1939).
(61) MEYER, T. M., AND KOOLHAAS, D. R.: Rec. trav. chim. **58**, 875 (1939).
(62) NAGAI, K.: J. Chem. Soc. Japan **23**, 740 (1902).
(63) ROARK, R. C.: J. Econ. Entomol. **24**, 328 (1931).
(64) ROARK, R. C.: U. S. Dept. Agr. Misc. Pub. 120 (1934); U. S. Dept. Agr. Bur. Entomol. Plant Quarantine, E-402 (1937), E-453 (1938) (mimeographed).
(65) ROARK, R. C.: J. Econ. Entomol. **34**, 684 (1941).
(66) ROBERTSON, A., AND RUSBY, G. L.: J. Chem. Soc. **1937**, 497.
(67) ROWAAN, P. A., AND DUUREN, A. J. VAN: Chem. Weekblad **35**, 755 (1938).
(68) SHEPARD, H. H., AND CAMPBELL, F. L.: J. Econ. Entomol. **25**, 142 (1932).
(69) SIEVERS, A. F., RUSSELL, G. A., LOWMAN, M. S., FOWLER, E. D., ERLANSON, C. O., AND LITTLE, V. A.: U. S. Dept. Agr. Tech. Bull. 595 (1938).
(70) SULLIVAN, W. N., GOODHUE, L. D., AND HALLER, H. L.: Soap **15** (7), 107 (1939).
(71) TAKEI, S., MIYAJIMA, S., AND ONO, M.: Ber. **66**, 1826 (1933).
(72) TATTERSFIELD, F., GIMINGHAM, C. T., AND MORRIS, H. M.: Ann. Applied Biol. **13**, 424 (1926).
(73) TATTERSFIELD, F., AND MARTIN, J. T.: Ann. Applied Biol. **22**, 578 (1935).
(74) TATTERSFIELD, F., AND MARTIN, J. T.: Ann. Applied Biol. **23**, 880 (1936).
(75) TATTERSFIELD, F., AND MARTIN, J. T.: J. Soc. Chem. Ind. **56**, 77T (1937).
(76) TATTERSFIELD, F., AND MARTIN, J. T.: Ann. Applied Biol. **25**, 411 (1938).
(77) TISCHLER, N.: J. Econ. Entomol. **28**, 215 (1935).