[Contribution from the Insecticide Division, Bureau of Chemistry and Soils]

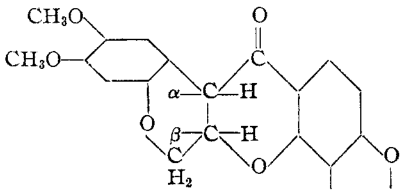
Rotenone. XXIX. The Isomerism of the Rotenolones[1]

By F. B. LaForge and H. L. Haller

The fish poisons and insecticidal constituents which have been isolated from various tropical Fabaceous plants are characterized chemically as derivatives of a substituted dihydrobenzo-γ-pyrone system containing two adjacent asymmetric carbon atoms. These substances may be classified in three groups. The rotenone group, of which rotenone itself is the only natural representative, has an optically active dihydrobenzofuran system, with an isopropenyl side chain joined to the dihydro-γ-pyrone system; the deguelin group, to which deguelin, tephrosin and isotephrosin belong, has an optically inactive dimethyldihydro-α-benzopyran system in place of the dihydrobenzofuran, and finally toxicarol, the only member of the third group, contains neither the dihydrobenzofuran nor the benzopyran system, but a grouping which is as yet unknown.

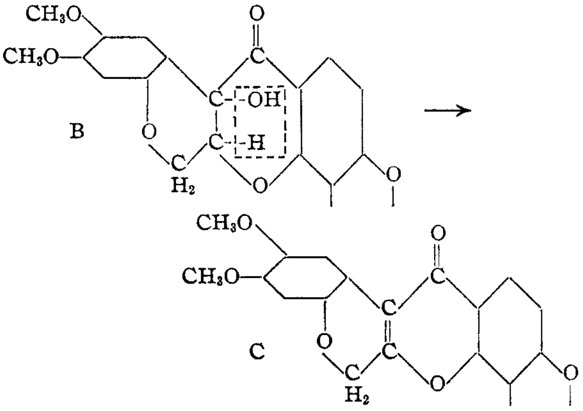
The structural formulas of both rotenone and deguelin have the grouping shown in formula A.

Tephrosin and isotephrosin have been shown to be monohydroxydeguelins in which the hydroxyl group is attached to the α or the β asymmetric carbon atom in the dihydro-γ-benzopyrone system.


A

They are related, therefore, to the rotenolones-I and -II, the hydroxy compounds corresponding to rotenone. Takei[2] is of the opinion that tephrosin and isotephrosin are not naturally present in the plants, but are formed by air oxidation in the presence of alkali employed in isolating them. Deguelin is in fact readily oxidized by air in alkaline alcoholic solution to a mixture of the two tephrosins.

There is nothing to indicate on which carbon atom the hydroxyl group is located in either the two rotenolones or the two tephrosins, although it has been assumed by Takei[3] that the hydroxyl of rotenolone-II is located on the β carbon atom of formula A. Both the two known rotenolones and the two known tephrosins are readily dehydrated by alcoholic mineral acids and by acetic anhydride to dehydrorotenone and dehydrodeguelin, respectively, as shown by the formulas B and C.


B

C

A third isomer of tephrosin, having the formula $C_{23}H_{22}O_7$, has now been obtained from deguelin by peroxide oxidation in alcoholic alkaline solution. This new isomer, which will be named hydroxydeguelin-C, melts at 203° and differs from tephrosin (m. p. 198°), especially in its behavior toward dehydrating agents. It is recovered unchanged after several hours of boiling with 8% alcoholic sulfuric acid. When acted upon by acetic anhydride and sodium acetate, it yields no dehydrodeguelin, but a colorless glassy material, probably the acetyl derivative, which however does not crystallize.

Rotenolone-I was first obtained from rotenone by oxidation with iodine in alcoholic solution containing potassium acetate.[4] It was later prepared by Takei,[3] together with rotenolone-II, by air oxidation of rotenone in the presence of alkali.

Peroxide oxidation of rotenone in the presence of alkali failed to yield a crystalline compound. Isorotenone, however, which is similar to deguelin in that it contains no asymmetric carbon atoms other than the two in the dihydro-γ-benzopyrone

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(1) For Rotenone XXVIII see *Ind. Eng. Chem.*, **25**, 983 (1933).

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

(3) Takei, Miyajima and Ono, *ibid.*, **66**, 479 (1933).

(4) LaForge and Smith, This Journal, **52**, 1091 (1930).

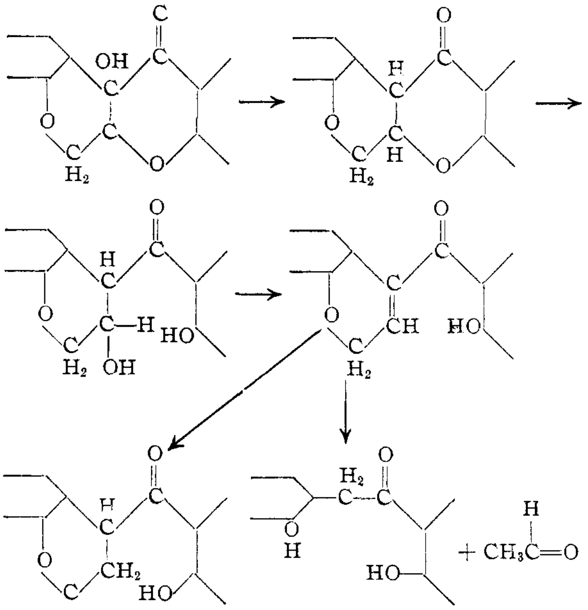
system, readily yields a compound having the formula $C_{23}H_{22}O_7$ on peroxide oxidation. This compound has been named isorotenolone-C. Another compound having the same formula, designated as isorotenolone-D, is also formed in small quantity in this reaction. These compounds as well as the corresponding deguelin derivatives are optically inactive.

Like the corresponding compound obtained from deguelin and unlike the two known rotenolones, isorotenolone-C and isorotenolone-D are completely stable to mineral acids, and no dehydroisorotenone is obtained even by prolonged boiling with 10% alcoholic sulfuric acid. By the action of acetic anhydride, isorotenolone-C is converted quantitatively into a crystalline monoacetyl derivative.

For comparison, the normal isorotenolones corresponding to rotenolones-I and -II have now been prepared, isorotenolone-I from isorotenone by the iodine oxidation method, and isorotenolone-II by air oxidation of isorotenone in the presence of alkali according to Takei's method.[3] These two compounds also show no optical activity. Isorotenolones-I and -II are both readily converted into dehydroisorotenone by boiling with alcoholic sulfuric acid, and the reaction proceeds at the same rate in each case.

As reported in a previous article,[4] rotenolone-I, like rotenone itself, is converted into derritol and rotenol by the action of zinc in alcoholic alkaline solution. It has also been shown that 2,2′-disubstituted benzoins are readily reduced by these reagents to desoxybenzoins.[5] Therefore it was concluded that rotenolone-I is a benzoin derivative with the hydroxyl on the carbon atom adjacent to the carbonyl group. It, therefore, would be expected that zinc in alkaline solution would reduce it to rotenone, after which the normal derritol–rotenol reaction[6] would proceed as shown.

Rotenolone-II is also reduced by zinc in alkaline alcoholic solution to derritol and rotenol and the yields are the same as in the case of rotenolone-I. By the same method, all four of the isorotenolones are also converted into isoderritol and isorotenol. The results obtained by zinc alkali reduction would indicate that all the rotenolones and isorotenolones are α-hydroxy compounds, because it is unlikely that if some were β-hydroxy compounds they would all show



Rotenol Derritol

identical behavior in this respect. Besides, it is difficult to explain the course of the derritol–rotenol reaction if the hydroxyl group is assumed to be located on the β-carbon atom. On the other hand, the number of isomers actually obtained is against the assumption that all are α-hydroxy derivatives.

Additional facts still more difficult to explain have been found in the properties of the methylated rotenolones. It has been shown that 2,2′-dimethoxybenzoin can be methylated easily by methyl iodide and silver oxide.[7] By this method, rotenolone-I and -II as well as all four isorotenolones yield quantitatively well-characterized methyl ethers.

Methylrotenolones-I and -II are converted with loss of methyl alcohol into dehydrorotenone by boiling with methyl alcoholic sulfuric acid. However, the reaction proceeds more slowly than the dehydration of the rotenolones under the same conditions.

When methylrotenolone-II is boiled for only a short time with methyl alcoholic sulfuric acid, it is converted largely to methylrotenolone-I, which is easily separated from the small quantity of dehydrorotenone formed.

Similarly methylisorotenolone-II is converted into methyl isorotenolone-I, and the latter is also easily freed from the dehydroisorotenone formed in the process. The two compounds rotenolone-II and isorotenolone-II are therefore

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[5] LaForge, THIS JOURNAL, **55**, 3040 (1933).

[6] LaForge and Haller, *ibid.*, **54**, 810 (1932).

[7] Irvine, *J. Chem. Soc.*, **79**, 670 (1901).

unstable forms. By long boiling with alcoholic sulfuric acid, methylrotenolones-I and -II and methylisorotenolones-I and -II are completely converted into dehydrorotenone and dehydroisorotenone, respectively.

When rotenolone-II or isorotenolone-II is allowed to stand for several days at room temperature in methyl alcohol containing a small quantity of hydrochloric acid, they are converted, respectively, into methylrotenolone-I and methylisorotenolone-I, together with the corresponding dehydro compounds. By the same treatment the dehydro compounds are unchanged. This conversion of the -II methyl into the -I methyl derivative furnishes definite proof that the methoxyl group in each pair is located on the same carbon atom and that a rearrangement on that atom has occurred, because a transfer of the methoxyl group from one carbon atom to the adjacent one could take place only with intermediate formation of the dehydro compound.

It may be safely assumed that a similar rearrangement of the hydroxyl of rotenolone-II and isorotenolone-II on its carbon atom occurs before they are dehydrated by alcoholic sulfuric acid. This assumption would exclude the explanation that isomerism among the four isorotenolones is due to *cis-trans* arrangement of the hydroxyl on one carbon with respect to hydrogen on the other.

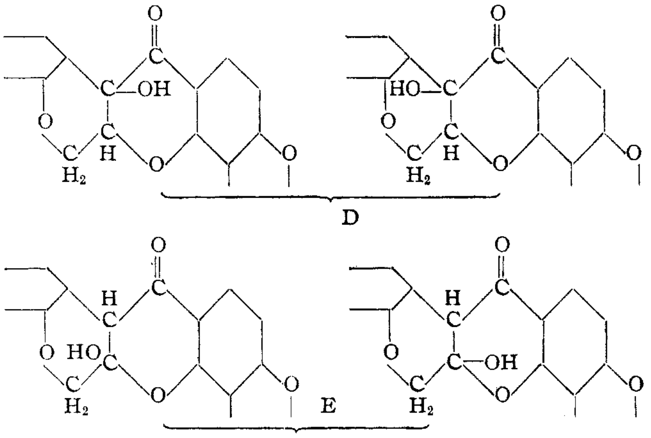
The methyl ethers of isorotenolones-C and -D are stable toward alcoholic sulfuric acid.

Methylrotenolones-I and -II, like the rotenolones themselves, undergo the derritol-rotenol reaction and yield derritol and rotenol. Also all four of the methylisorotenolones give good yields of isoderritol and isorotenol.

We have found in this connection that 2,2′-dimethoxybenzoin methyl ether like 2,2′-dimethoxybenzoin itself is converted quantitatively into 2,2′-dimethoxydesoxybenzoin by zinc in alcoholic alkaline solution. Thus an analogy is presented to show that a methoxyl group in the position α to the carbonyl group can be removed by reduction, but there is no evidence that a similar reaction might not occur if the methoxyl group occupied the β position in the methyl rotenolones.

The positions of hydroxyl groups in tephrosin, isotephrosin and hydroxydeguelin-C, in the rotenolones-I and -II, and in the isorotenolones-I, -II, -C and -D therefore remain undecided.

It can be stated definitely only with respect to rotenolones -I and -II and isorotenolones -I and -II, that these compounds constitute pairs with the hydroxyl on the same carbon atom, which may be represented by one or the other of formula types D and E.



The same relation probably holds between tephrosin and isotephrosin.

It will be noted that the α and β carbon atoms in formula A are combined with two-ring systems on one side and three on the other, and therefore several planes of asymmetry may be present on both sides of the axis joining these two asymmetric centers. This unique condition may produce combinations of optical and geometric isomerism which are different for each of the observed rotenolones.

Such an assumption would include the possibility of a number of isomers of other rotenone and deguelin derivatives, and the number would be further increased by the presence of another asymmetric center in such compounds as rotenone or dihydrorotenone.

Experimental

Hydroxydeguelin-C.—Five grams of deguelin (m. p. 171°) was dissolved in 65 cc. of 5% methyl alcoholic potassium hydroxide, the solution was warmed on the steam-bath, and 10 cc. of 30% hydrogen peroxide was added in small portions. With the first additions of peroxide, the solution turned black but the color soon changed to light yellow. The heating was continued for about half an hour. After a short time at room temperature, crystallization began. The product was removed by filtration, washed with methyl alcohol, and recrystallized by dissolving in a small quantity of chloroform, adding methyl alcohol and concentrating the solution until the chloroform was removed. The compound crystallized in prisms which melted at 203°. The yield of recrystallized material was 3.5 g.

Anal. Calcd. for $C_{23}H_{22}O_7$: C, 67.30; H, 5.41; $2CH_3O$, 15.12. Found: C, 67.17, 66.97; H, 5.55, 5.47; CH_3O, 15.56, 15.59

Unlike deguelin or rotenone, the compound did not absorb iodine in alcoholic potassium hydroxide solution and was recovered unchanged after boiling for several hours with this reagent.

It was also recovered unchanged in practically quantitative yield after boiling for five hours with ten parts of 8% alcoholic sulfuric acid.

Isorotenolone-C.—Isorotenone gave a corresponding new hydroxy derivative under experimental conditions the same as those employed in the case of deguelin except that less peroxide was used. Five grams of isorotenone in 65 cc. of 5% methyl alcoholic potassium hydroxide when oxidized with 7 cc. of 30% hydrogen peroxide yielded 3.2 g. of isorotenolone-C. After several recrystallizations, made by dissolving in chloroform, adding methyl alcohol and concentrating, the compound, which crystallized in plates, melted at 212° (analysis in Table I).

After several hours of boiling with 10% alcoholic sulfuric acid, 80% of the material was recovered unchanged. It was also unaffected by boiling with 5% alcoholic potassium hydroxide and by heating for half an hour at 220°.

Acetylisorotenolone-C.—One gram of isorotenolone-C was boiled for fifteen minutes on reflux with 5 cc. of acetic anhydride and 0.2 g. of anhydrous sodium acetate to which a few drops of acetic acid had been added. The acetic anhydride was destroyed by the addition of a few cc. of methyl alcohol, water was added, and the amorphous material was separated and dissolved in methyl alcohol. It crystallized at once and was recrystallized from about ten parts of methyl alcohol. It melted at 145–146°.

Anal. Calcd. for $C_{25}H_{24}O_8$: C, 66.35; H, 5.31; $2CH_3O$, 13.71. Found: C, 65.98, 66.16; H, 5.26, 5.33; CH_3O, 13.78.

Isorotenolone-D.—This compound is formed in small quantity when isorotenone is oxidized with peroxide to obtain isorotenolone-C. It sometimes crystallizes in aggregates of large prisms, which may be separated mechanically. When recrystallized by dissolving it in a little chloroform, adding methyl alcohol and concentrating, it melted at 188–189° (analysis in Table I).

Isorotenolone-I.—Twelve grams of isorotenone was dissolved in 300 cc. of absolute alcohol containing 30 g. of potassium acetate. An alcoholic solution of iodine was dropped in as long as it was decolorized. About 8 g. of iodine was used.

On standing, about 7 g. of dehydroisorotenone separated out. This was removed, the solution was concentrated on the water-bath, and cold water was added. The precipitated amorphous material was removed by filtration and dissolved in ether, and the ether was evaporated, leaving a light yellow sirup which weighed about 5 g. The sirupy acetyl derivative was dissolved in about 30 cc. of 3% methyl alcoholic potassium hydroxide solution, and the solution was boiled for one hour. On standing, isorotenolone-I crystallized from the reddish-brown solution and was recrystallized by dissolving it in a large volume of methyl alcohol, decolorizing with carbon and concentrating the filtered solution. The yield was only about 0.4 g. of crude material. When again recrystallized it melted at 203–204° (analysis in Table I).

It was readily converted into isodehydrorotenone by boiling with 10% alcoholic sulfuric acid. When mixed with an authentic sample of isodehydrorotenone the melting point was 196–197°.

Isorotenolone-II.—Ten grams of finely ground isorotenone was suspended in 250 cc. of 95% alcohol, 7 cc. of *N* potassium hydroxide was added, and a rapid stream of air was passed through the suspension for about three hours. During the reaction the suspended material changed to a heavy granular precipitate. After standing

TABLE I

No.	Substance	Crystal form	M. p., °C.	Found, %[a]		
				C	H	CH_3O
1	Rotenolone-I	Heavy prisms	140	[a]	[a]	[a]
2	Rotenolone-II	Plates	220	[a]	[a]	[a]
3	Isorotenolone-I	Flat prisms	203–204	66.88	5.39	15.41
4	Isorotenolone-II	Heavy prisms	193–194	67.34	5.40	15.36
5	Isorotenolone-C	Flat plates	210–212	67.36	5.42	15.59
6	Isorotenolone-D	Heavy prisms	188–189	66.80	5.61	15.57

No.	Action of alcoholic H_2SO_4	Zinc and alkali reduction	M. p., °C.	Action of CH_3I and Ag_2O	Action of MeOH–HCl
1	Dehydrorotenone	Derritol	163	Methylrotenolone-I	Methylrotenolone-I
		Rotenol	121		
2	Dehydrorotenone	Derritol	163	Methylrotenolone-II	Methylrotenolone-I
		Rotenol	120–121		
3	Dehydroisorotenone	Isoderritol	149	Methylisorotenolone-I	
		Isorotenol	132–133		
4	Dehydroisorotenone	Isoderritol	148	Methylisorotenolone-II	
		Isorotenol	134		
5	Isorotenolone-C	Isoderritol	150	Methylisorotenolone-C	
		Isorotenol	133		
6	Isorotenolone-D	....	...	Methylisorotenolone-D	

[a] Calculated values for the rotenolones and isorotenolones ($C_{23}H_{22}O_7$): C, 67.30; H, 5.41; CH_3O, 15.1. The analyses for rotenolone-I and rotenolone-II have been reported in previous articles.

overnight, this was separated, washed and dried. The yield was 7.6 g. and an additional 1 g. was obtained by concentrating the mother liquor. This material melted at 190–192°, but the melt did not clear until the temperature was raised to 200°. It is a mixture of isorotenolone-I and -II, in which the latter predominates. After three recrystallizations, made by dissolving the material in a small quantity of chloroform and adding methyl alcohol, it melted at 193–194° (analysis in Table I).

One-half gram of isorotenolone-II boiled for four hours with 10% alcoholic sulfuric acid gave 0.3 g. of dehydroisorotenone, m. p. 197–198°. It was identified by comparison with an authentic sample of isodehydrorotenone as to melting point and optical properties of the crystals.

Isoderritol and Isorotenol from Isorotenolone-C.—Two grams of isorotenolone-C was boiled for three and a half hours with 30 cc. of 15% aqueous potassium hydroxide, 70 cc. of alcohol and 5 g. of zinc dust. The solution was filtered from the zinc, acidified and extracted with ether. The ethereal solution was washed with water and extracted three times with 2% alkali. On acidification, the alkaline solution yielded 1.4 g. of isoderritol. After recrystallization it melted at 149°. The product mixed with authentic isoderritol melted at 150°. The ethereal solution after removal of the isoderritol yielded on evaporation 0.1 g. of material, which crystallized on moistening with methyl alcohol. When recrystallized from methyl alcohol, it melted at 133°. Mixed with isorotenol, it melted at 133°.

Under the same conditions, rotenolone-II yielded derritol and rotenol, and isorotenolones-I and -II isoderritol and isorotenol. Also under the same conditions, methylrotenolones-I and -II yielded derritol and rotenol, and methylisorotenolones-I, -II and -D, isoderritol and isorotenol.

Zinc Alkali Reduction of Hydroxydeguelin-C.—When hydroxydeguelin-C was treated with zinc and alcoholic alkali and the reaction product was separated into alkali soluble and insoluble fractions, no crystalline products could be obtained from either fraction. Both products, however, gave phenol reactions with ferric chloride, indicating that a similar reaction had occurred. Under the same conditions of treatment, deguelin itself also fails to give crystalline products analogous to derritol and rotenol.

Methyl Ethers of the Rotenolones and Isorotenolones.—All the rotenolones and isorotenolones were methylated by the method used by Irvine[7] for the methylation of 2,2′-dimethoxybenzoin. The following is an example. One gram of rotenolone-I was boiled for one hour with about 12 cc. of methyl iodide and 3.5 g. of dry silver oxide. The silver oxide was added in several portions during the reaction. Ether was added and the solution was filtered from the silver compounds and evaporated. The colorless residue crystallized after a short time, and the material was recrystallized from methyl alcohol. The same proportions were employed in the methylation of rotenolone-II and all four of the isorotenolones. The reaction can be carried out with very small quantities of material. This was necessary for instance in the case of isorotenolone-I where 0.17 g. of substance gave 0.12 g. of recrystallized methyl derivative. In all cases the yield was nearly quantitative. Isorotenolones-C and -D required about two hours of boiling to complete the reaction.

Isorotenolone-I is difficult to obtain in quantity by the iodine method, and it cannot be isolated in pure condition from the mixture obtained by air oxidation. However, pure methyl isorotenolone-II is readily obtained by methylation of the crude product obtained by air oxidation and is easily freed from the more soluble methylisorotenolone-I. Methylisorotenolone-I in turn is obtained pure by transformation of methylisorotenolone-II by alcoholic sulfuric acid and is easily freed from the almost insoluble dehydroisorotenone which is simultaneously formed.

The properties and reactions of the rotenolones are summarized in Table I and those of the methyl rotenolones in Table II.

Table II

No.	Substance	Crystal form	M. p., °C.	CH_3O found[a]
1	Methylrotenolone-I	Long white rods	174–175	21.94
2	Methylrotenolone-II	Short white prisms	148–149	21.92
3	Methylisorotenolone-I	White needles	153	21.68
4	Methylisorotenolone-II	Short yellow prisms	133–134	21.73
5	Methylisorotenolone-C	Short heavy white prisms	160–161	22.12
6	Methylisorotenolone-D	Short white prisms	190–191	22.08[b]

[a] Calculated values for the methylrotenolones and methylisorotenolones ($C_{24}H_{24}O_7$): (3) CH_3O, 21.94.

[b] Calculated for $C_{24}H_{24}O_7$: C, 67.89; H, 5.70. Found: C, 67.38; H, 5.75.

No.	Action of methyl alcoholic H_2SO_4 (2 hrs.)	Action of methyl alcoholic H_2SO_4 (20 min.)	Zinc and alkali reduction	M. p., °C.
1	Dehydrorotenone	Dehydrorotenone + Methylrotenolone-I	Derritol Rotenol	160 119–120
2	Dehydrorotenone	Dehydrorotenone + Methylrotenolone-I	Derritol Rotenol	159–162 120–121
3	Dehydroisorotenone	Dehydroisorotenone + Methylisorotenolone-I	Isoderritol Isorotenol	148–149 132
4	Dehydroisorotenone	Dehydroisorotenone + Methylisorotenolone-I		
5	Methylisorotenolone-C		Isoderritol Isorotenol	148–151 133–134
6	Methylisorotenolone-D		Isoderritol Isorotenol	148–149 132–133

Zinc Alkali Reduction of 2,2'-Dimethoxybenzoin Methyl Ether to 2,2'-Dimethoxydesoxybenzoin.—One and three-tenths g. of 2,2'-dimethoxybenzoin methyl ether[7] was boiled for three hours with 15 cc. of 15% aqueous potassium hydroxide, 45 cc. of alcohol and 3 g. of zinc dust. The solution was filtered from zinc, acidified, diluted and extracted with ether. The ether solution was washed with water, dried and evaporated. The ether residue crystallized on seeding with 2,2'-dimethoxydesoxybenzoin. The yield was quantitative. A part was recrystallized from petroleum ether and melted at 57°, which is in agreement with the figure reported for dimethoxydesoxybenzoin.[5]

Anal. Calcd. for $C_{16}H_{16}O_3$: $2CH_3O$, 24.21. Found: CH_3O, 24.01, 23.91.

Summary

A new hydroxy derivative of deguelin has been prepared by peroxide oxidation in alcoholic alkali solution. The compound is isomeric with the two known tephrosins, but, unlike these, it is not dehydrated by mineral acids. By the same method a corresponding compound isorotenolone-C has been obtained from isorotenone together with another isomer, isorotenolone-D both of which are also stable to dehydrating agents.

Isorotenolones-I and -II corresponding to the normal rotenolones were obtained by the iodine method and by air oxidation of isorotenone. Isorotenolones-I and -II are dehydrated by mineral acids yielding dehydroisorotenone.

All four isorotenolones are converted into their methyl ethers by silver oxide and methyl iodide.

Methyl isorotenolone-II is transformed into methyl isorotenolone-I by acids but methyl isorotenolone-C and -D are stable.

The four isorotenolones-I, -II, -C and -D all undergo the derritol-rotenol reaction and yield isoderritol and isorotenol.

From the facts presented, it appears that isorotenolone-II is an unstable form having the methoxyl group on the same carbon atom as methyl isorotenolone-I. It is not possible to decide whether the hydroxyl group in the isorotenolones is located on the alpha or beta carbon atom of the dihydro-γ-benzopyrone system. The isomerism of the four isorotenolones may be due to a combination of optical and geometric isomerism due to the presence in the several compounds of different planes of asymmetry of the ring systems joined to the two asymmetric carbon atoms in the dihydro-γ-pyrone systems.

WASHINGTON, D. C. RECEIVED MAY 3, 1934

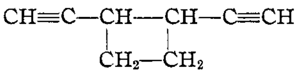
[CONTRIBUTION NO. 130 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXI. Polymerization of Vinylacetylene

BY HARRY B. DYKSTRA

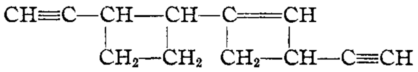
The facts that vinylacetylene is the simplest possible enyne and is conjugated confer some importance on a knowledge of its polymerization. In the first paper of this series,[1] it was reported that the polymerization of vinylacetylene in the presence of cuprous chloride gave a dimer, "acetylene tetramer," which was considered to be octatriene-1,5,7-yne-3. Thermal polymerization, on the other hand, was stated to convert vinylacetylene into viscous drying oils and finally into hard resinous solids. It was suggested that this reaction involved only the ethylenic linkages and resulted in a chain bearing primary acetylenic groups at alternate carbons.

While a decisive demonstration of the structure of the thermal polymers of vinylacetylene is extraordinarily difficult, some evidence has now been obtained that the above view is incorrect; the products more likely consist of cyclobutane and cyclobutene derivatives, such as I, II and III.



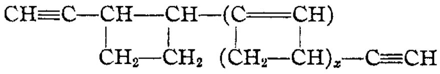
$$\begin{array}{ccccc} CH\equiv C- & CH & - & CH & -C\equiv CH \\ & | & & | & \\ & CH_2 & - & CH_2 & \end{array}$$

I



$$\begin{array}{ccccccccc} CH\equiv C- & CH & - & CH & - & C & = & CH & \\ & | & & | & & | & & | & \\ & CH_2 & - & CH_2 & & CH_2 & - & CH & -C\equiv CH \end{array}$$

II



$$\begin{array}{ccccccccc} CH\equiv C- & CH & - & CH & - & (C & = & CH) & \\ & | & & | & & | & & | & \\ & CH_2 & - & CH_2 & & (CH_2 & - & CH)_x & -C\equiv CH \end{array}$$

III

A very unexpected observation made in the course of this study was that the thermal polymerization of vinylacetylene in the presence of certain acidic materials, *e. g.*, acids, acid anhydrides and phenols, leads to the formation of styrene. Resinous products are also formed, but under suitable conditions approximately one-half of the polymer consists of the dimer, styrene.

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[1] Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197 (1931).