

been removed completely. The crude product weighed 0.022 g. One-half of the material was recrystallized from ethyl acetate; m. p. 173–174°.

Phenyldichloroarsine reacts in an analogous manner.

Anal. Calcd. for $C_{18}H_{26}S_4N_2As$: As, 15.87; S, 27.15. Found: As, 15.76; S, 26.92.

Summary

Diarylarsyl and diarylstibyl iodides react readily with the piperidine salt of N-pentamethylenedithiocarbamic acid to form N-pentamethylene-S-diarylarsyl- and N-pentamethylene-S-diarylstibyl dithiourethans. Unlike the triarylmethyl analogs these substances do not undergo spontaneous decomposition in solution to form compounds of the type $R_2As-AsR_2$ and $R_2Sb-SbR_2$. Phenyldihaloarsines and the piperidine salt of the dithiourethan interact to yield a dithiocarbamate. Because of the advantageous properties of this substance the piperidine salt of the dithiocarbamic acid is suggested as a reagent for the identification of small quantities of alkyl- and aryl dihaloarsines.

ANN ARBOR, MICHIGAN

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

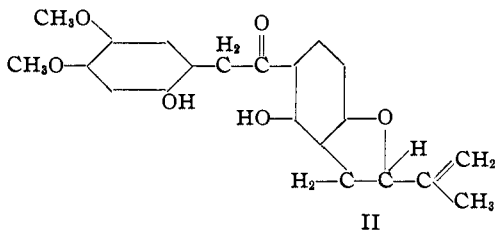
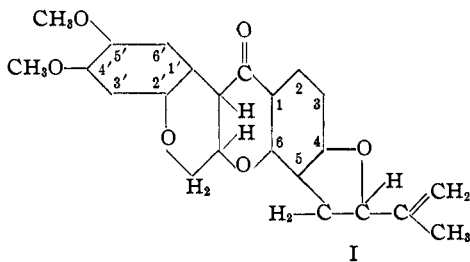
ROTENONE. XXII. SOME NEW DATA IN CONFIRMATION OF THE STRUCTURE OF ROTENONE

BY L. E. SMITH AND F. B. LAForge

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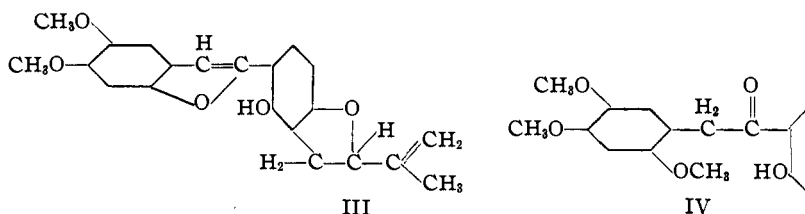
The complete formula for rotenone having been established on the basis of its principal reactions as I,¹ reference should be made to several other typical reactions not explained in previous articles.



¹ LaForge and Haller, *THIS JOURNAL*, **54**, 810 (1932).

Derritol has been shown to correspond to the formula II¹ and analogous structures apply to its derivatives, iso- and dihydroderritol.

The derritols are converted into anhydroderritols with loss of one molecule of water. The reaction mechanism proposed by Butenandt for this transformation has proved to be correct, and anhydroderritol therefore corresponds to the formula III.² The reaction is, however, best accomplished by boiling the compounds in xylene solution with phosphorus pentoxide rather than by distillation as recommended by Butenandt. The anhydroderritols all contain a free phenolic hydroxyl group in position 6 and can be acetylated to monoacetyl compounds which do not give the ferric chloride reaction. They are insoluble in alkali, a property which is in agreement with the fact that all phenols of the rotenone series with only one hydroxyl group in the 6 position, are alkali insoluble.¹



The methyl derritols, IV, do not yield anhydrides although they give the color reaction with ferric chloride and are easily acetylated to compounds which do not give the test. It has already been observed that the derritols themselves give two moles of hydrogen by the Zerewitinoff method.²

All these relations serve as further confirmation of formula III for derritol.

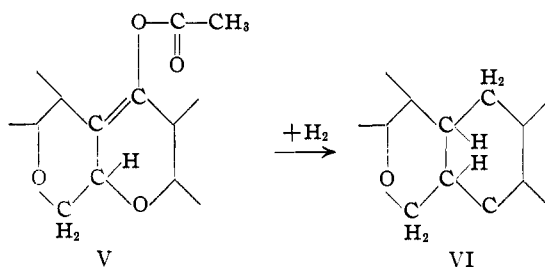
As previously reported, dehydrodihydrorotenonic acid is easily acetylated in position 4 to a monoacetyl compound. From analogy it could be predicted that dihydrorotenonic acid would yield a corresponding monoacetyl derivative. Contrary to expectations, however, treatment of dihydrorotenonic acid with acetic anhydride and sodium acetate resulted in the formation of a diacetyl derivative.

Rotenone, dihydrorotenone and isorotenone on treatment with acetic anhydride yielded monoacetyl compounds.

These results might have been very disturbing in the speculations on the structure of rotenone, had they been observed before the rotenone formula had been established. They are, however, easily explained on the assumption that rotenone and rotenonic acid react to form enol acetates, V. This theory has been proved definitely by the fact that on catalytic hydrogenation acetyldihydrorotenone is easily converted into dihydrodesoxyrotenone, VI, with simultaneous loss of the acetyl group.³ The enol acetates

¹ Butenandt, *Ann.*, **464**, 253 (1929).

³ Roll and Adams, *THIS JOURNAL*, **53**, 8469 (1931).



of rotenone and dihydrototenone give promise of being of practical importance owing to their comparative stability toward oxidation. Comparative toxicity tests are being made on these compounds. The structure of rotenonone will be discussed in a future communication.

Experimental

The Anhydrotentritols.—Two grams of substance was dissolved in 75 cc. of xylene and 4 g. of phosphorus pentoxide was added in small portions to the boiling solution. The solution was then decanted from the viscous residue and evaporated to dryness on the steam-bath. The crude product crystallized on cooling. The yield in all cases was about 1.5 g.

Anhydro.	Recrystallized from	M. p. °C.	Ferric chloride test	Formula	Analyses, %			
					Calcd. C	H	Found C	H
Derritrol	CH ₃ OH	160	Red	C ₂₁ H ₂₀ O ₅	71.55	5.72	71.74	5.80
Isoderritrol	CH ₃ OH	149	Red	C ₂₁ H ₂₀ O ₅	71.55	5.72	71.79	5.72
Dihydroderritrol	Dil. MeOH	164	None	C ₂₁ H ₂₂ O ₅	71.18	6.21	71.04	6.39

The Acetylanhydrotentritols.—One gram of substance, 0.2 g. of anhydrous sodium acetate and 10 cc. of acetic anhydride were refluxed for two hours. When the solution was poured into water the substance was obtained crystalline. The yield in all cases was about 1 g. Acetyldihydroderritrol methyl ether was obtained by the same method.

No.	Name	Recrystallized from	M. p., °C.	Ferric chloride test	Analyses, %							
					Calcd. C	H	CH ₃ CO	OCH ₃	Found C	H	CH ₃ CO	OCH ₃
1	Acetylanhydrotentritol	CH ₃ OH	146	None								
2	Acetylanhydroisoderritrol	C ₂ H ₅ OH	158	None								
3	Acetylanhydrodihydroderritrol	C ₂ H ₅ OH	138	None								
4	Acetyldihydroderritrol methyl ether	C ₂ H ₅ OH	98	None								

No.	Formula	Calcd.		Analyses, %					
		C	H	CH ₃ CO	OCH ₃	Found C	H	CH ₃ CO	OCH ₃
2	C ₂₃ H ₂₂ O ₆	70.05	5.58			70.07	5.51		
3	C ₂₃ H ₂₄ O ₆	69.69	6.06			69.73	6.02		
4	C ₂₄ H ₂₅ O ₇	67.28	6.54	10.04	21.72	67.33	6.64	10.41	21.71
									21.46

Diacyldihydrotentenonic Acid.—One gram of dihydrotentenonic acid, 0.3 g. of anhydrous sodium acetate and 16 cc. of acetic anhydride were refluxed for one hour, and the solution then evaporated to dryness on the steam-bath. The product was washed with water and then recrystallized from dilute ethyl alcohol. The substance melted at 115–116°. It was again recrystallized from petroleum ether (b. p. 80–100°) and it

then melted at 119°; yield, 0.8 g. Calcd. for $C_{27}H_{30}O_8$: C, 67.22; H, 6.22; $2CH_3O$, 12.86; $2CH_3CO$, 17.84. Found: C, 67.62, 67.23; H, 5.91, 6.15; CH_3O , 13.17, 12.87; CH_3CO , 17.79.

This same compound was obtained when 2 g. of dihydrorotenonic acid dissolved in 5 cc. of pyridine was treated in the cold with 1 g. of acetyl chloride. After standing at room temperature for three days, water was added and the mixture extracted with ether. The ether extract was extracted twice with water, twice with 10% hydrochloric acid and once with 10% potassium carbonate solution. After drying over anhydrous sodium sulfate the ether was evaporated and the product recrystallized from petroleum ether, m. p. 119°. When the substances obtained by the two methods were mixed, the melting point was not depressed.

The Acetylrutenones.—One gram of substance, 0.3 g. of anhydrous sodium acetate and 16 g. of acetic anhydride were refluxed for one hour, and the solution was then evaporated to dryness on the steam-bath. After washing with water the products were recrystallized. The compounds can also be prepared by the pyridine-acetyl chloride method as in the case of diacetyldihydrorotenonic acid. Acetylisorotenone is distinctly yellow in color whereas the corresponding rotenone and dihydrorotenone derivatives are only very slightly colored.

	Re-crystal- lized from	M. p., °C.	Formula	Analyses							
				Calcd.				Found			
				C	H	CH_3CO	OCH_3	C	H	CH_3CO	OCH_3
Acetyldihydro- rotenone	C_8H_8OH	209– 211	$C_{27}H_{30}O_7$	68.49	5.93	9.86	14.15	68.48	6.11	9.68	14.26
Acetylrutenone	C_8H_8OH	135	$C_{25}H_{24}O_7$	68.8	5.5		14.22	68.97	5.75		14.17
Acetylisorotenone	C_8H_8OH	144	$C_{25}H_{24}O_7$	68.8	5.5		14.22	68.75	5.58		14.22

Dihydrodesoxyrotenone from Acetyldihydrorotenone.—Four-tenths gram of acetyldihydrorotenone in acetic acid solution was reduced with hydrogen under 50 pounds pressure with 0.2 g. of platinum oxide catalyst. The substance crystallized when the acetic acid solution was diluted with water. It was filtered off, dissolved in ether, and the ether solution was extracted with 5% potassium hydroxide. The ether solution was then dried over anhydrous sodium sulfate and evaporated to dryness. The product was recrystallized from methyl alcohol; m. p. 168°, yield 0.3 g. When mixed with dihydrodesoxyrotenone there was no depression of melting point.

*Anal.*⁴ Calcd. for $C_{23}H_{26}O_5$: C, 72.28; H, 6.86. Found: C, 72.23, 72.08; H, 6.97, 7.05.

Summary

Anhydroderritols were prepared from derritol, isoderritol and dihydroderritol by the action of phosphorus pentoxide on the xylene solution of the corresponding derritols.

The methyl derritols do not yield anhydrides.

The anhydroderritols are alkali insoluble but give ferric chloride color reactions and can be acetylated.

The mechanism of the formation of the anhydroderritols proposed by Butenandt has proved to be correct. These reactions serve as a confirmation of the derritol formula as previously proposed. Dihydrorotenonic acid gives a diacetyl derivative. Rotenone, isorotenone and dihydrorotenone give monoacetyl compounds. These acetyl compounds belong to

⁴ These analyses were made by Mr. J. R. Spies of this division.

the class of enol acetates and one of the acetyl groups in dihydrorotenonic acid is of this type.

Dihydrorotenone monoacetate is reduced by catalytic hydrogen to dihydrodesoxyrotenone.

WASHINGTON, D. C.

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

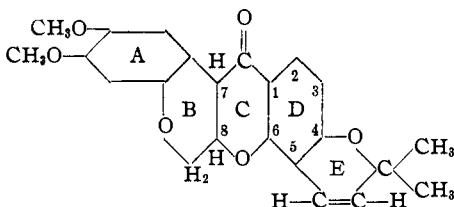
DEGUELIN. IV. THE STRUCTURE OF DEGUELIN AND TEPHROSIN

BY E. P. CLARK

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PUBLISHED JULY 6, 1932

On the basis of information now available it may be stated with a considerable degree of assurance that the structure of deguelin is represented by formula I.



I. Deguelin, $C_{28}H_{22}O_6$

This statement is based upon facts concerning reactions of deguelin previously published together with certain new information which will be presented at this time and also upon the important observation previously made relative to relationships existing between deguelin and rotenone.

As the reactions principally involved in establishing that portion of the structure of deguelin represented by rings A, B, C and D have been recorded¹ and an interpretation of these reactions has been made in establishing the same structures in toxicarol,² it will be necessary only to refer to these facts briefly.

Deguelin, like rotenone and toxicarol, contains two hydrogen atoms which are readily removed by mild oxidation. In their place a double bond is introduced into the molecule, and the oxidation product, dehydrodeguelin (formula II), undergoes reactions which establish the fact that the position of the new double bond is between the carbon atoms common to rings B and C (designated in the formula as carbon atoms 7 and 8). The facts supporting the last statement are as follows: first, permanganate oxidation of dehydrodeguelin yields three products, namely, 2-hydroxy-4,5-dimethoxybenzoic acid, risic acid (2-carboxy-4,5-dimethoxyphenoxyacetic

¹ Clark, *THIS JOURNAL*, (a) **53**, 313 (1931); (b) **53**, 2369 (1931); (c) **53**, 3431 (1931); (d) **53**, 2007 (1931).

² Clark, *ibid.*, **54**, 2537 (1932).