each of which has been characterized as a diacetate and triacetate.

3. Perbenzoic acid titrations and non-reactivity with maleic anhydride indicate the presence of two non-conjugated, active double bonds in both osajin and pomiferin.

4. By a combination of the Wilson boric acid color reaction and the Asahina reduction tests, it is shown that a flavanone structure for hexahydro-osajin and a flavone structure for osajin and pomiferin are probable.

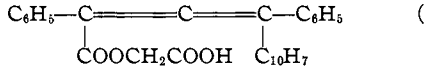
Columbus, Ohio Received April 8, 1940

[Contribution from the Chemical Laboratories of Harvard University]

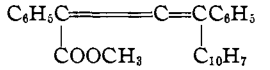
Optically Active α,γ-Diphenyl-α-carbomethoxy-γ-naphthylallene

By Elmer P. Kohler and Wendell J. Whitcher[1]

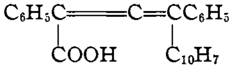
The glycolic acid ester of α,γ-diphenyl-γ-naphthylallene carboxylic acid (I) was recently


$C_6H_5\text{—}\underset{COOCH_2COOH}{C}=C=\underset{C_{10}H_7}{C}\text{—}C_6H_5$ (I)

resolved in this Laboratory,[2] and we now describe the preparation and behavior of the optically active forms of the corresponding allenic methyl ester (II).

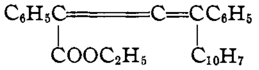

$C_6H_5\underset{COOCH_3}{C}=C=\underset{C_{10}H_7}{C}C_6H_5$ (II)

The solid inactive glycolic acid ester (I), with diazomethane, yielded its methyl derivative, but the active forms of (I), on similar treatment, or when subjected to hydrolysis in the attempt to prepare active forms of the simple allenic acid (III), gave only oily products.


$C_6H_5\underset{COOH}{C}=C=\underset{C_{10}H_7}{C}C_6H_5$ (III)

The optically active methyl esters of the simple allenic acid (II), however, were synthesized by at least two of the following methods: (1) the active glycolic acid ester (I) was hydrolyzed by a large excess of alcoholic potassium hydroxide, the active form of the simple allenic acid (III) was converted into the silver salt, and the latter, with methyl iodide, to the active methyl ester (II); (2) the active allenic acid (III), prepared by the hydrolysis of active (I), was treated with diazomethane and yielded the active methyl ester (II); and (3) the active glycolic acid ester (I) was converted to the active methyl ester (II) by absolute methyl alcoholic potassium hydroxide.

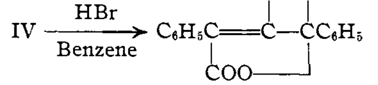
A study of the formation of the active and inactive methyl esters (II) by the third method, as well as the rapid conversion of the inactive glycolic acid ester (I) to the inactive ethyl ester (IV)


$C_6H_5\underset{COOC_2H_5}{C}=C=\underset{C_{10}H_7}{C}C_6H_5$ (IV)

by ethyl alcoholic potassium hydroxide, indicated that the reaction proceeded by ester interchange. The pure methyl esters (II) were obtained in yields increasing with the amount of potassium hydroxide used up to two equivalents. With 1.1 mole of potassium hydroxide (0.08 *M*), during one hour, 62% yield of methyl ester was obtained, but 80% was obtained with two moles (0.25 *M*) during a quarter hour. The sign of rotation of each optically active ester was the same as that of the parent glycolic ester no matter which method of transformation was employed.

That these enantiomeric methyl esters retained the allenic system was demonstrated by dissolving together equimolecular quantities of each in ether, and isolating from the solution only an inactive ester which proved to be identical with the inactive methyl ester (II) prepared by a method leaving no doubt as to its structure.[2]

Solutions of the active forms of the glycolic acid ester (I) and of the methyl ester (II) in benzene and in ethyl acetate remained optically active during long periods when kept in the dark, but on exposure to sunlight for a few days the solution developed a yellow color, became inactive, and the inactive form of (I) or (II) (50–60% yield) was isolated together with a yellow resin.


$\mathrm{IV}\xrightarrow[\text{Benzene}]{\text{HBr}}C_6H_5\underset{COO\text{—}}{C}=\overset{H}{C}\text{—}\overset{C_{10}H_7}{\underset{\text{—}}{C}}C_6H_5$ (V)

It has been shown that the inactive ethyl ester (IV) with hydrogen bromide in benzene solution yields the crotono lactone[3] (V).

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[1] The experimental work described in this manuscript was completed before the death of Professor Kohler. The present manuscript has been prepared since that time by the junior author.

[2] Kohler, Walker and Tishler, This Journal, **57**, 1743 (1935).

[3] Unpublished work of Dr. Max Tishler

Whereas analogous treatment of the active methyl esters (II) seemingly offered an unprecedented opportunity for the conversion of a molecule with asymmetry due to its structure as a whole into one in which asymmetry is dependent upon a particular carbon atom, the dextro methyl ester, when subjected to this treatment, underwent ring closure as expected, but with complete loss of activity, and only the inactive form of the crotono lactone could be isolated.

Experimental Part

The Methyl Ester of the Glycolic Acid Ester, $C_6H_5C(COOCH_2COOCH_3){=}C{=}C(C_{10}H_7)C_6H_5$.—An ether solution of 2.0 g. of inactive glycolic acid ester (I) was treated with enough diazomethane to esterify 1.2 g. Excess acid ester was removed by sodium bicarbonate extraction and 0.92 g. of crystalline methyl ester was recovered, m. p. 113°.

Anal. Calcd. for $C_{29}H_{22}O_4$: C, 80.16; H, 5.11. Found: C, 80.28; H, 5.32.

Active Methyl Esters of α,γ-Diphenyl-γ-naphthylallene Carboxylic Acid (II). (1) **By Way of the Silver Salt.**—Hydrolysis of 0.5 g. of levo glycolic acid ester (I) was carried out with excess alcoholic potassium hydroxide. The alcoholic solution was diluted with water, acidified with nitric acid and extracted with ether, from which extract any glycolic acid or unhydrolyzed acid ester was removed by aqueous sodium bicarbonate. The levo allenic acid (III) was taken up in aqueous sodium hydroxide and converted into the silver salt in the manner previously employed[2] in the case of the inactive acid. Boiling the salt with excess methyl iodide in ether led to isolation of 0.16 g. of levo methyl ester (II), m. p. 91°, $[\alpha]_D$ −49.8° in benzene at 25°.

Anal. Calcd. for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36. Found: C, 86.14; H, 5.62.

(2) **By Means of Diazomethane.**—An ether solution of the active form of (III) prepared as above from 0.5 g. of the levo glycolic acid ester (I) when dried and treated with an equivalent quantity of diazomethane deposited 0.1 g. of levo methyl ester (II).

(3) **By Action of Potassium Hydroxide in Methyl Alcohol.**—A solution of 1.32 g. of dextro glycolic acid ester (I) in 25 cc. of a 0.25 *M* solution of potassium hydroxide in absolute methyl alcohol was boiled for fifteen minutes, poured into water and the aqueous solution extracted with ether. Ether and petroleum ether deposited 0.94 g. of the dextro methyl ester, m. p. 91°, $[\alpha]_D$ +49.3° in benzene at 25°.

Conversion of Active Ester to Crotono Lactone (V).—When 0.159 g. of the dextro methyl ester (II) was dissolved in 10 cc. of benzene containing 0.085 g. of hydrogen bromide, the rotation fell rapidly, practically disappearing in twenty minutes. From this solution was recovered 0.10 g. of the crotono lactone (V), m. p. 189°, readily identified by comparison with an authentic sample. A series of such conversions indicated that the rate and extent of lactone formation was dependent on the initial concentration of the hydrogen bromide.

Summary

Although the enantiomeric forms of α,γ-diphenyl-γ-naphthyl-allene carboxylic acid have not been obtained in the solid state, the crystalline methyl esters of this acid have been obtained from the active forms of its glycolic acid ester by three methods: (a) hydrolysis and subsequent treatment with diazomethane, (b) hydrolysis, formation of the silver salt of the acid, and subsequent reaction with methyl iodide, and (c) ester interchange in methyl alcoholic potassium hydroxide.

Whereas acids rapidly isomerize the above acid and its alkyl esters to a crotono lactone with one asymmetric carbon atom, the coversion of the active methyl esters to this lactone by hydrogen bromide in benzene was accompanied by loss of optical activity.

CAMBRIDGE, MASS.

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