Calcd. for $C_{22}H_{22}$: C, 92.3; H, 7.7. Found: C, 92.3; H, 8.2. In view of the violence of the Grignard reaction, it is improbable that the ethylphenanthrene derives from unchanged Grignard compound. It could have been formed by dismutation of the expected carbinol, or when methylcyclopentanone inclines to react in an enolic form.[11]

Summary

1. Cyclopentenotriphenylene has been prepared, starting with β-(9-phenanthryl)-ethyl chloride and cyclopentanone.
2. The nature of several by-products has been discussed.

REHOVOTH, PALESTINE RECEIVED APRIL 9, 1936

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[11] Compare Grignard and Savard, *Bull. soc. chim. Belg.*, **36**, 97 (1927).

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Cerin and Friedelin. III. A Study of the Oxidative Degradation of Friedelin[1]

BY NATHAN L. DRAKE AND WILLIAM P. CAMPBELL

Our previous study of cerin and friedelin[2] has shown that these substances are polycyclic in nature, the former a hydroxy ketone, the latter a ketone, both derived from the same nucleus. From evidence now available[3] it is apparent that this polycyclic nucleus contains five fused rings, and that cerin and friedelin are derived from a completely hydrogenated picene, and should be classed as derivatives of a triterpene.

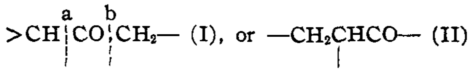
It is the purpose of this communication to describe certain degradation experiments in which the attack on the friedelin molecule is at the carbonyl group.

Sodium and amyl alcohol reduce friedelin to the corresponding alcohol, friedelinol, whose benzoate can be prepared readily by the action of benzoyl chloride on the alcohol in pyridine solution. This benzoate, when heated in an atmosphere of nitrogen to 300°, is converted into a hydrocarbon friedelene, $C_{30}H_{50}$, and benzoic acid. Similar unsaturated hydrocarbons with alkyl or aryl groups attached to the carbon which, in the original friedelin molecule, held the carbonyl oxygen, can be prepared by the action of the Grignard reagent on friedelin. Phenylmagnesium bromide yields such a hydrocarbon directly; the tertiary alcohol first produced undergoes spontaneous dehydration. Two products are obtained when methylmagnesium iodide reacts with friedelin. One is the expected methyl-substituted tertiary alcohol, the other methylfriedelene. The tertiary alcohol is readily dehydrated by acetic anhydride to methylfriedelene. All of these unsaturated substances give a pronounced yellow color with tetranitromethane, but the *purest* friedelin gives no color.

The ready dehydration which these alcohols undergo, and the formation of benzoic acid from the benzoate, prove the presence of a hydrogen atom adjacent the carbonyl group of friedelin, and indicate that this hydrogen is probably tertiary.

Because friedelene is so easily accessible it was chosen for further study. Oxidation of friedelene by chromic anhydride in glacial acetic acid yields a neutral substance, $C_{30}H_{48}O$. This compound gives a color with tetranitromethane and yields no methane when treated with methylmagnesium iodide. The substance $C_{30}H_{48}O$ must, therefore, be an unsaturated ketone, and since no methylene group of friedelin behaves in a similar fashion during oxidative degradations, it is reasonable to assume that the ketone $C_{30}H_{48}O$, which we have called friedelenone, owes its formation to the activating effect of the double bond on the hydrogens of an adjacent methylene group. The formation of α,β-unsaturated ketones by oxidation is a common reaction in the terpene series. Pinene can be oxidized to verbenone by treatment with chromic acid[4] and cedrin[4] and limonene can also be converted to α,β-unsaturated ketones by oxidation.[5] Similarly cholestene is converted to cholestenone under the influence of chromic anhydride.[6]

On the basis of this evidence the existence of the grouping



$$>\mathrm{CH}\overset{a}{\vdots}\mathrm{CO}\overset{b}{\vdots}\mathrm{CH_2}\text{— (I), or —}\mathrm{CH_2}\underset{|}{\mathrm{C}}\mathrm{HCO}\text{— (II)}$$

in friedelin is postulated. Evidence obtained from the oxidation of friedelin makes it possible

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[1] From the Ph.D. dissertation of William P. Campbell.

[2] Drake and Jacobsen, THIS JOURNAL, **57**, 1570: Drake and Shrader, *ibid.*, 1854 (1935).

[3] *Cf.* the fourth article in this series, *ibid.*, **58**, 1684 (1936).

[4] Semmler and Jakubowicz, *Ber.*, **47**, 1143 (1914).

[5] Blumann and Zeitschel, *ibid.*, **47**, 2624 (1914).

[6] Windaus, *ibid.*, **53**, 488 (1920).

to assign the partial structure (I) to one ring of the friedelin molecule.

Friedelin is oxidized by chromic anhydride in glacial acetic acid mainly to a keto acid containing thirty carbon atoms $C_{30}H_{50}O_3$, for which we propose the name friedonic acid. The neutralization equivalent of the acid, the saponification equivalent of its methyl ester, and determination of its carbon and hydrogen content are all in accord with the formula written. It is obvious, therefore, that friedonic acid is produced by the opening of a hydroaromatic ring which holds some substituent on the carbon adjacent to the carbonyl group. Although it has not proved possible to obtain from this acid any derivatives by replacement of the carbonyl oxygen, it is possible to reduce friedonic acid to a neutral substance, $C_{30}H_{50}O_2$, the lactone of an hydroxy acid. In accord with this interpretation are the neutrality of the reduction product, the fact that it gives no color with tetranitromethane, thus excluding simple dehydration of an hydroxy acid with formation of an unsaturation, and its saponification equivalent. We propose to call this substance the lactone of friedolic acid.

In addition to friedonic acid, a keto acid containing twenty-nine carbon atoms is produced by the oxidation of friedelin.

It has proved impossible thus far to separate the more soluble C_{29} keto acid as such from the C_{30} acid, for both crystallize very poorly, but reduction of the more soluble fractions obtained during purification of the C_{30} acid yields a mixture of lactones from which that of the C_{29} acid can be separated. Analyses and determinations of saponification equivalent demonstrate the formula of this lactone to be $C_{29}H_{48}O_2$; it is therefore norfriedolo lactone.

The simplest interpretation of these reactions considered in conjunction with the oxidation of friedelene to friedelenone is that during the oxidation of friedelin the structure (I) is cleaved at (a) and at (b) forming, respectively, friedonic acid and a dibasic acid which, because it contains the grouping $>CH-$ adjacent to the carboxyl is very easily degraded further, yielding norfriedonic acid.

There is ample justification in the literature for the assumption that the intermediate dibasic acid would readily undergo further degradation, for isobutyric acid yields acetone when treated with hydrogen peroxide or chromic acid,[7] and methylheptylacetic acid is degraded by chromic acid to methyl heptyl ketone.

Oxidation of friedelene produces a very small acidic fraction, from which by reduction with sodium and alcohol norfriedolo lactone, identical with the compound obtained by oxidation of friedelin, is obtained. It should be stated that the evidence on which the identity of this acidic oxidation product of friedelene is based consists of a determination of the melting point of the compound mixed with norfriedolo lactone obtained from friedelin. This sort of evidence appears to be admissible in the light of our experience with other degradation products of friedelin.

Norfriedonic acid is formed, then, from friedelenone by cleavage of the ketone at the double linkage and further degradation of the α-keto acid so produced. The formation of norfriedonic acid in this reaction proves that the methylene group in friedelin must be adjacent to the carbonyl and not as represented in (II). Thus it is clear that the carbon which is lost in the formation of norfriedonic acid is the one which held the carbonyl oxygen in friedelin.

Experimental

Friedelinol.—To 1 g. of friedelin dissolved in 100 ml. of boiling *n*-amyl alcohol was added 2 g. of sodium. Refluxing was continued until the sodium had dissolved, whereupon the solvent was removed by distillation with steam, and the product crystallized from benzene–ethyl acetate or from amyl alcohol. Friedelinol crystallizes in hexagonal plates which melt 301–304°. The yield of friedelinol prepared from pure friedelin was 90%. When so called "friedelin-rich"[8] material is reduced, the yield is 50–65%, but this lower yield actually represents a larger friedelinol yield based on "friedelin-rich" substance, for a considerable loss is entailed in purifying friedelin through its enol ester.

Anal. Calcd. for $C_{30}H_{52}O$: C, 84.03; H, 12.23. Found: C, 83,81, 83.75; H, 12.10, 12.08.

Friedelinyl Iodide.—Friedelinol (0.5 g.), red phosphorus (0.2 g.), and iodine (1.3 g.) were heated in dry benzene under reflux for three hours. The warm solution was shaken with mercury to remove excess iodine and evaporated to 5 ml. *in vacuo*. Water was added, the benzene removed *in vacuo*, and the product recrystallized from benzene. Leaching with a small quantity of benzene removed contaminating mercuric iodide, whereupon recrystallization from benzene–ethyl acetate resulted in a product which melted with decomposition at 224–226°.

Anal. Calcd. for $C_{30}H_{51}I$: I, 23.57. Found: I, 23.59, 23.36.

The molecular weights of friedelin calculated from these analyses are 426 and 432, respectively. These values

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[7] Schmidt, *Ber.*, **7**, 1363 (1874).

[8] *Cf.* paper I, THIS JOURNAL, **57**, 1571 (1935).

are in excellent agreement with those obtained from the saponification equivalents of certain enol esters of friedelin (*cf.* paper I).[8] The calculated molecular weight for $C_{30}H_{50}O$ is 426.

Friedelinyl Methyl Ether.—Friedelinol (0.04 g.) in methyl iodide (20 ml.) was heated under reflux for several hours with silver oxide. The solution was filtered, and the ether obtained by evaporation of the methyl iodide. After recrystallizations from ethyl acetate, from which the ether crystallizes in plates, the product melted at 265–267°.

Anal. Calcd. for $C_{31}H_{54}O$: C, 84.09; H, 12.30. Found: C, 84.04; H, 12.25.

Friedelinyl Acetate.—Friedelinol (1 g.) was heated for two hours under reflux in 100 ml. of acetic anhydride. The acetate which separated in long lath-like plates when the solution was cooled, was recrystallized from benzene. The product melted at 315–316°.

Anal. Calcd. for $C_{32}H_{54}O_2$: C, 81.63; H, 11.57. Found: C, 81.46, 81.55; H, 11.65, 11.55.

Friedelinyl Benzoate.—To a boiling solution of friedelinol (2.8 g.) in dry pyridine (125 ml.) was added benzoyl chloride (15 ml.). After the solution had been heated under reflux for one-half hour, 300 ml. of 95% ethanol was added and the solution allowed to cool to room temperature. The substance which separated was recrystallized from a benzene–alcohol mixture. Friedelinyl benzoate crystallizes in long laths which melt at 250–251°.

Anal. Calcd. for $C_{37}H_{56}O_2$: C, 83.39; H, 10.59. Found: C, 83.43, 83.29; H, 10.56, 10.71.

Friedelene.—Friedelinyl benzoate (5 g.) was heated in an atmosphere of nitrogen at 280–320° for three and one-half hours. The benzoic acid was removed from the product by 10% aqueous sodium hydroxide. After purification by crystallization from ethyl acetate–benzene the substance melted at 257–258°. It crystallizes in lath-like plates, and gives a yellow color with tetranitromethane.

Anal. Calcd. for $C_{30}H_{50}$: C, 87.72; H, 12.28. Found: C, 87.89, 87.98; H, 12.37, 12.26.

Attempts to dehydrate friedelinol directly by use of sulfuric acid, oxalic acid, sodium bisulfate, phosphorus pentachloride and thionyl chloride yielded products which would not crystallize.

Phenylfriedelene.—To a solution of phenylmagnesium bromide, prepared in ethyl ether from 25 ml. of bromobenzene and 6 g. of magnesium, was added an equal volume of dry benzene. This solution of Grignard reagent was then mixed at room temperature with a solution of 5 g. of friedelin in 500 ml. of dry benzene. To complete the reaction the mixture was heated under reflux for one-half hour. The crude product, obtained by pouring the solution into dilute acid and removing the benzene by steam distillation, was recrystallized several times from ethyl acetate from which it separated in the form of thin plates, which melted at 269–271°.

Anal. Calcd. for $C_{36}H_{54}$: C, 88.82; H, 11.18. Found: C, 88.84, 88.97; H, 11.26, 11.30.

Only 0.3 g. of phenylfriedelene was obtained; the balance of the reaction products was a gum which would not crystallize, and would not react with acetic anhydride to yield a crystalline product.

Methylfriedelinol.—This compound was prepared from 5 g. of friedelin by a method quite similar to that described directly above. The crude solid product was leached with 250 ml. of a boiling ethyl acetate–benzene mixture (2:1). Methylfriedelinol crystallized from the leachings, and after further purification by crystallization from benzene a product which crystallized in lath-like hexagonal plates, and melted at 316–319°, was obtained.

Anal. Calcd. for $C_{31}H_{54}O$: C, 84.09; H, 12.30. Found: C, 83.98, 84.19; H, 12.43, 12.42.

A small quantity of methylfriedelene was obtained from the residue left by the leaching process described above.

Methylfriedelene.—Methylfriedelinol was dehydrated by heating it under reflux in an acetic anhydride solution containing a little xylene to render the alcohol more soluble. After about two hours, a part of the solvent was removed by distillation, and the product which separated on cooling was recrystallized from benzene and ethyl acetate to constant melting point. Methylfriedelene crystallizes in hexagonal plates which melt at 272–274°.

Anal. Calcd. for $C_{31}H_{52}$: C, 87.65; H, 12.35. Found: C, 87.65, 87.70; H, 12.36, 12.47.

Oxidation of Friedelene to Friedelenone.—Friedelene (3.6 g.) dissolved in acetic acid (900 ml.) was oxidized at 97° by chromic anhydride (2.4 g.). After six hours 500 ml. of water and a little methanol were added, the mixture boiled for a few minutes and filtered; 3.5 g. of light green solid separated on cooling. This substance was dissolved in ether and shaken with 10% sodium hydroxide solution to remove any acidic fraction. The ether layer was separated and evaporated until crystallization started. The substance so obtained melted at 290–291° after one recrystallization from ether. Friedelenone crystallizes from ether in lath-like plates apparently monoclinic, which are easily differentiated under a petrographic microscope from all of the other oxidation products herein described. Friedelenone is the only oxidation product thus far examined which shows oblique extinction; the extinction angle measured from the long side of the crystal is approximately 24°.

Anal. Calcd. for $C_{30}H_{48}O$: C, 84.83; H, 11.40. Found: C, 84.83, 84.83; H, 11.32, 11.36.

Friedelenone gave a pronounced yellow color with tetranitromethane, and when treated with methylmagnesium iodide in amyl ether evolved no methane.

Acidification of the alkaline extract mentioned above produced 1.5 g. of amorphous solid. To this solid, dissolved in 50 ml. of boiling *n*-propyl alcohol, was added 3 g. of sodium cut in small pieces. When all of the sodium had dissolved, the solution was diluted with 500 ml. of water and acidified. The substance which separated was crystallized from ethyl acetate to yield a very small quantity of a compound which melted 287–289°. A mixture of this substance with norfriedolo lactone obtained from friedelin (m. p. 289–291°) melted at 288–289°.

Oxidation of Friedelin to Friedonic Acid.—Chromic anhydride (2.4 g.) dissolved in glacial acetic acid (125 ml.) was added slowly over a period of about four hours to a suspension of 5 g. of friedelin in 600 ml. of boiling glacial acetic acid. The mixture was heated under reflux for an additional eleven hours, during which time the friedelin gradually dissolved. After about two-thirds of the solvent had been removed by distillation, 500 ml. of water was added to the hot solution. After cooling and filtering, the solid was dissolved in ether, and shaken with 10% sodium hydroxide. Sodium salts precipitated in the aqueous layer and were rendered compact at the ether-water interface by the use of a centrifuge. The ether solution was separated and the mixture extracted with a fresh portion of ether. From the combined ether extracts was obtained 0.8 g. of friedelin and 0.2 g. of a resinous material.

The aqueous layer was made acid to Congo red paper, warmed to coagulate the acids and filtered. By recrystallization from aqueous alcohol and finally from 95% alcohol 1.3 g. of a product, which crystallized in narrow laths and melted 206–207°, was obtained.

Anal. Calcd. for $C_{30}H_{50}O_3$: C, 78.54; H, 11.00. Found: C, 78.83, 78.75; H, 10.91, 11.02. *Neutral Equiv.* Calcd. for $C_{28}H_{49}(CO)(COOH)$: 458. Found: 463, 461.

Methyl Friedonate.—This ester was prepared from the crude acid fraction obtained by oxidation of friedelin as above. Esterification was accomplished by heating the sodium salt in absolute ethanol with excess methyl iodide. Methyl friedonate crystallizes from methyl alcohol in narrow laths which melt at 249–251°.

Anal. Calcd. for $C_{31}H_{52}O_3$: C, 78.75; H, 11.09. Found: C, 78.60, 78.85; H, 11.21, 11.42. *Sapon. Equiv.* Calcd. for $C_{29}H_{49}(CO)(COOCH_3)$: 472. Found: 473, 471.

Friedolo Lactone and Norfriedolo Lactone.—Two and four-tenths grams of the lower melting crude acid fraction obtained from the oxidation of friedelin was dissolved in 140 ml. of *n*-propyl alcohol. This solution was heated under reflux and 6 g. of sodium cut in small pieces was added. When all the sodium had dissolved, the solution was diluted with 500 ml. of water, cooled and filtered. The resulting solid was crystallized from ethyl alcohol (160 ml.) and then several times from ethyl acetate. Friedolo lactone crystallizes from ethyl acetate in rods, which melt 309–312°.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.37; H, 11.39. Found: C, 81.24, 81.12; H, 11.26, 11.25.

The alcoholic filtrate from the first crystallization mentioned above was evaporated to half its volume, cooled and filtered. The crystals which separated were purified by further recrystallization from ethyl acetate. The compound norfriedolo lactone crystallizes from ethyl acetate in long needle-like laths, and melts 289–291°. This melting point is considerably depressed by admixture of friedolo lactone.

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.24; H, 11.30; sapon. equiv., 428. Found: C, 81.09, 81.29; H, 11.29, 11.34; sapon. equiv., 431, 429.

We should like to acknowledge our indebtedness to R. P. Jacobsen for his analyses of friedelinyl iodide, and to J. R. Spies for analyses of friedelinol and friedelinyl methyl ether.

Summary

1. The oxidation of friedelin and friedelene by chromic anhydride in glacial acetic acid has been studied, and from evidence so obtained the structure $CHCOCH_2$- in the friedelin molecule is deduced.

2. The preparation of friedelinol and of several of its derivatives is described.

3. Several acidic and neutral degradation products of friedelene and friedelin have been prepared.

COLLEGE PARK, MD. RECEIVED JUNE 25, 1936

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Cerin and Friedelin. IV. The Dehydrogenation of Friedelinol[1]

BY NATHAN L. DRAKE AND WILLARD T. HASKINS

In continuation of our studies on the structure of cerin and friedelin, we have subjected friedelinol to dehydrogenation by selenium in order to determine the type of aromatic nucleus to which friedelin is related. Friedelinol rather than friedelin was chosen for study because previous investigation had shown that friedelin, like most ketones whose carbonyl forms a part of a ring system, yielded products too complex and too far removed from the original nuclear structure to be a satisfactory substance for dehydrogenation studies.

The products obtained from friedelinol by dehydrogenation are 1,2,7-trimethylnaphthalene (sapotalene), 1,2,8-trimethylphenanthrene, a hydrocarbon $C_{25}H_{20}$, apparently identical with a polymethyl picene isolated by Ruzicka and coworkers from the dehydrogenation products of a number of triterpenes,[2] and a liquid hydrocarbon, $C_{11}H_{20}$, which has the properties of an alkyl substituted cyclohexene.

The evidence advanced by Ruzicka[3] in support of a picene nucleus in the hydrocarbon $C_{25}H_{20}$ is quite conclusive; consequently there must be in cerin and friedelin a pentacyclic nucleus of the

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(1) From the Ph.D. dissertation of W. T. Haskins.

(2) Ruzicka, Frame, Leicester, Liguori and Brüngger, *Helv. Chim. Acta*, **17**, 426 (1934).

(3) Ruzicka, Hösli and Ehmann, *ibid.*, **17**, 445 (1934).