

THE OXIDATIVE DEGRADATION OF FRIBOELIN

By

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of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy.

1936.

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INTRODUCTION

Earlier work by Drake and Jacobsen¹ and Drake and Shrader² has shown that friedelin is a polycyclic ketone possessing the formula $C_{30}H_{50}O$. It is the purpose of this research to ascertain the nature of the groups attached to the carbon atoms adjoining the carbonyl group. The method of attack adopted involves oxidation of the molecule at the carbonyl group, isolation of the products of these reactions, and interpretation of the results thus obtained.

DISCUSSION

Friedelin is reduced almost quantitatively by the action of metallic sodium and amyl alcohol to the corresponding alcohol, friedelinol. This substance forms an acetate when heated with acetic anhydride alone whereas friedelin undergoes no reaction under the same conditions. Methyl iodide and silver oxide convert the carbinol to a methyl ether. By heating with benzoyl chloride or by the action of benzoyl chloride in pyridine a benzoate is formed. Phosphorus and iodine convert friedelinol to an iodide $C_{30}H_{51}I$. Analysis of this substance for iodine provides an additional check on the molecular weight of friedelin. The average value from these analyses is 428 as compared to the average value of 425 obtained by Drake and Jacobsen¹.

Of the several methods of attacking the problem of degradation of the friedelin molecule, which were considered, two seemed most feasible. The first was to introduce a double bond into the molecule at the carbonyl carbon atom, and to split the molecule by oxidation with chromic acid or ozone. In order that the method be useful it is necessary that the unsaturated compound be capable of

preparation in fairly good yield. To this end, several unsaturated hydrocarbons were prepared.

Friedelin on treatment with phenyl magnesium bromide forms an unsaturated hydrocarbon of the formula $C_{30}H_{49}C_6H_5$. However, the yield of crystalline material from this reaction is very low. The name, phenylfriedelene is proposed for this compound.

Two products can be obtained from the reaction of friedelin with methyl magnesium iodide; friedelin methyl carbinol, $C_{31}H_{54}O$, and an unsaturated hydrocarbon, methyl friedelene, $C_{31}H_{52}$. The presence of an unsaturation in the hydrocarbon is shown by the color produced with tetranitromethane. Friedelin methyl carbinol is converted to methyl friedelene very easily by boiling with acetic anhydride.

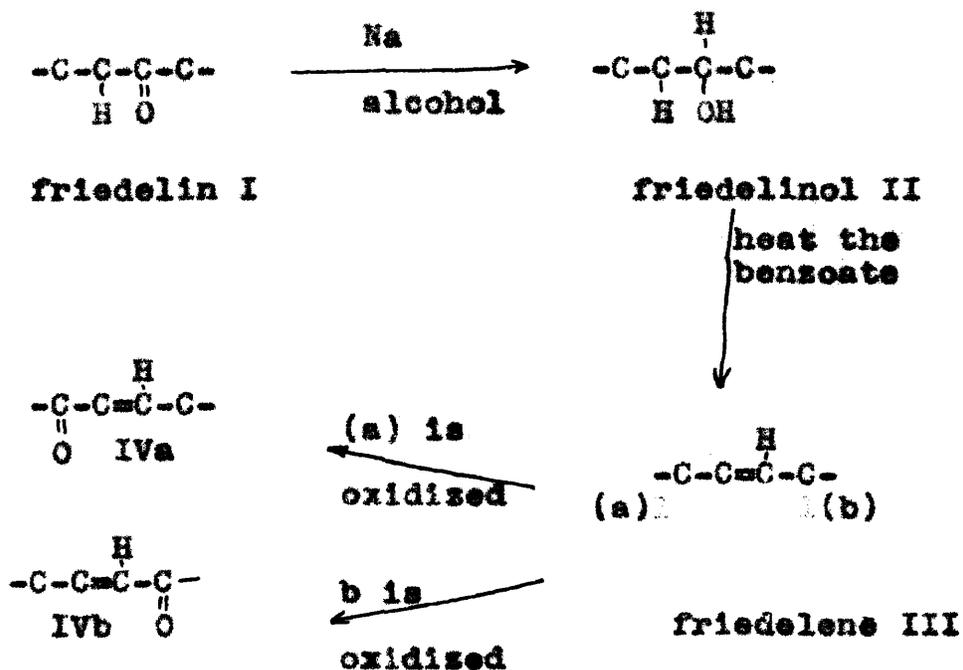
A third method of introducing a double bond into the molecule involves heating friedelinyl benzoate at 280° to 320° in an atmosphere of nitrogen. A molecule of benzoic acid is eliminated from the benzoate producing the hydrocarbon friedelene, $C_{30}H_{50}$, in 84% yield.

Of these three hydrocarbons friedelene was chosen for oxidative degradation since it is easily prepared and does not contain any synthetically added carbon atoms. When friedelene is oxidized with chromic acid in glacial

acetic acid a neutral substance which analyzes for $C_{30}H_{48}O_2$ is formed. The analytical results eliminate the possibility that the substance results from cleavage of the double bond, since the carbon content of these products would be considerably lower than that required by $C_{30}H_{48}O$. Since the substance gives the tetranitromethane test for unsaturation and since it does not produce any methane when treated with methyl magnesium iodide; it is concluded that it is an unsaturated ketone.

Studies of the oxidation of friedelin with chromic acid fail to show any methylene group that is oxidized directly to a carbonyl. Thus the methylene group in friedelene appears to be activated by the double bond. The direct oxidation of a methylene group to a carbonyl has been observed in several alicyclic compounds where the group is activated by an adjacent double bond. For example pinene can be oxidized to verbenone by treatment with chromic acid³ or elementary oxygen⁴. Likewise cedrin³, and limonene⁵ can be oxidized to alpha-beta unsaturated ketones. The methylene group adjacent to the double bond in cholestene is converted to a carbonyl by the action of chromic acid.⁶ On the basis of this evidence the carbonyl group is placed adjacent to the double bond.

The formation of friedelene from the benzoate proves the presence of at least one hydrogen on a carbon atom adjacent to the carbonyl group of friedelin. The oxidation of friedelene to an alpha-beta unsaturated ketone proves that one of the carbon atoms adjacent to the double bond holds two hydrogen atoms. Thus the reactions are as follows:



The decision between these two formulas (IVa and IVb) for the unsaturated ketone can be made on the basis of evidence obtained from the oxidation of friedelin. By treatment with chromic acid in glacial acetic acid, friedelin is oxidized mainly to a keto-acid containing thirty carbon atoms which we propose to call suberonic acid.

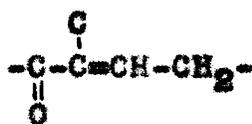
The formula, $C_{30}H_{50}O_3$, is established by analysis and by determination of the molecular weight by neutralization equivalent of the acid and saponification equivalent of the methyl ester. The presence of a carbonyl group is demonstrated by reduction of the substance with sodium and alcohol to form a neutral compound $C_{30}H_{50}O_2$. The formula corresponds to that of the expected hydroxy acid from which one molecule of water has been eliminated. If the water had split out to form an unsaturation the substance would not be neutral. In addition, it does not give the tetranitromethane test for unsaturation. The only conclusion that can be drawn from this evidence is that the compound is the lactone of the hydroxy acid which is formed when the carbonyl of the keto acid is reduced to an hydroxoxyl group. The name given to the hydroxy acid is suberolic acid.

In addition to suberonic acid, a keto acid containing twenty-nine carbon atoms is formed on oxidation of friedelin. This substance can be isolated only as the lactone which is formed on reduction of the crude acid fraction from the oxidation. Analysis and saponification equivalent indicate the formula $C_{29}H_{48}O_2$ for the lactone. The name suggested for this substance is norsuberolo-lactone.

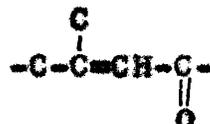
that on oxidation the acid is first converted to the ketone.



These reactions prove that one of the carbon atoms adjacent to the carbonyl in friedelin is a methylene group, and that the other holds a tertiary hydrogen. Formulas IVa and IVb representing the unsaturated ketone can then be rewritten (Va and Vb).



Va



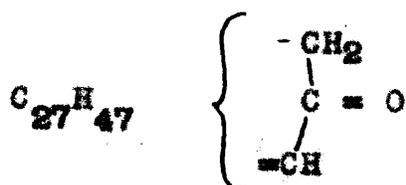
Vb

When friedelene is oxidized to produce the unsaturated ketone a small acid fraction is obtained. On reduction of this fraction with sodium and alcohol a substance is obtained identical with the norsuberolo-lactone from the oxidation of friedelin. It must be noted that this identity is established on the basis of mixed melting point. Although this rule is not without exceptions¹⁰, it has been successfully used with many compounds in this research.

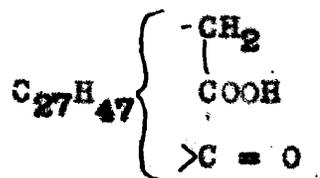
The norsuberolo-lactone obtained from friedelene is undoubtedly formed by oxidation of the unsaturated

ketone (Va or Vb) eliminating the carbon atom between the double bond and the carbonyl. If formula Va were correct, further oxidation could produce only a dibasic or tribasic acid. Whereas formula Vb would be expected to produce norsuberonic acid. Therefore formula Vb is correct and the name friedelenone is proposed for the unsaturated ketone.

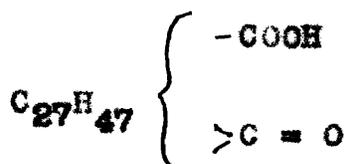
Thus friedelin, suberic acid, norsuberonic acid, and friedelenone can be formulated as follows:



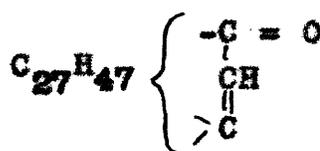
friedelin



suberic acid



norsuberonic acid



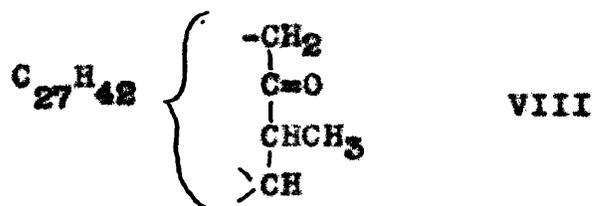
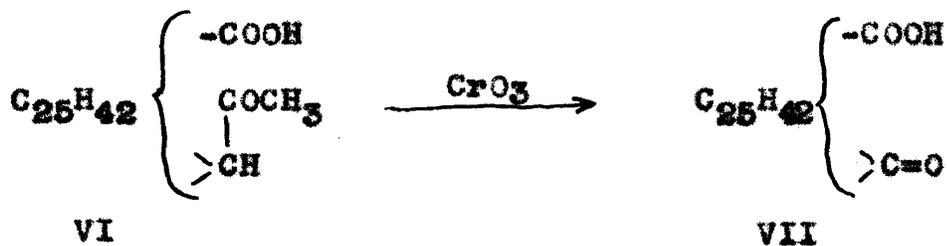
friedelenone

Attempts to prepare an oxime and a 2,4-dinitrophenylhydrazone of suberic acid failed. This may be due to a highly blocked carbonyl. The lower melting fractions of crude acid obtained by oxidation of friedelin could not be crystallized from any solvent. However, a method of purification of doubtful value was devised. The substance

is dissolved in a little ethyl alcohol and partially precipitated as sodium salt by the addition of 10% sodium hydroxide solution. The precipitate is filtered and dissolved in aqueous alcohol. This solution and the filtrate are diluted with about ten times their volume of water, acidified with hydrochloric acid, and warmed on the steam bath to coagulate the precipitates. If the concentration of alcohol in these solutions is too high, coagulation results in a sticky mass. Of the two crops obtained by this method, one should contain more of the acid which forms the least soluble sodium salt. From a solution of these fractions in ethyl alcohol, a viscous oil is precipitated either by cooling or by adding water. After the oil has settled the solution is poured off. White solid is obtained from the oil and the solution by treating the alcoholic solution with alkali, diluting with water, acidifying and heating to coagulate the precipitate. The solid obtained in this manner from the precipitated oil should contain more of the least soluble acid. By applying both of these separations to the low melting crude acid, a substance melting at 121-124° is obtained. The melting point could not be changed by further treatment.

Analysis and neutralization equivalent of this

substance indicate the formula $C_{27}H_{44}O_3$, a keto acid. The formation of this acid is easily explained if norsuberonic acid is written with a CH_3CO group as in formula VI. Then, by oxidation, two carbon atoms are removed and the C_{25} keto-acid (VII) is produced



On the basis of this evidence friedelin is represented by formula VIII. It must be noted however that the C_{27} acid could not be obtained in crystalline form, and due to the nature of the method of purification further evidence is necessary to establish this formula with certainty.

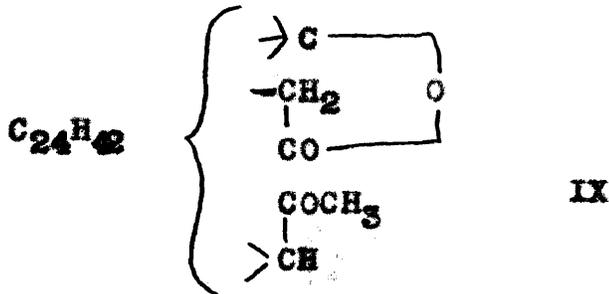
Several attempts were made to show that suberonic acid contains a CH_3CO group. Considerable difficulty was met in carrying out the iodoform reaction on the acid. It is necessary to use a half of a gram of acid in order to obtain an appreciable quantity of iodoform. In alkaline

solution the acid forms a thick gel unless the solution is diluted to such a point that the concentration of the reagents become very small. Agitation of the solution produces a rigid foam which prevents thorough mixing of the reagents. In addition, the iodine-potassium iodide solution salts out sodium suberonate. The odor of iodoform can be detected in the residue left on evaporation of the ether extract of the reaction mixture but it cannot be isolated in a quantity sufficient for melting point determination.

Suberonic acid appears to react with sodium hypobromite producing an oil, which on treatment with methyl iodide and silver oxide, is converted to a crystalline solid. At the close of this research this substance had not been prepared in sufficiently large quantities for identification. This work, however, indicates that further study of these reactions may prove the presence of a CH_3CO group in suberonic and norsuberonic acids, thereby lending support to the formula proposed for the C_{27} keto acid.

By vigorous oxidation of friedelin with chromic acid a compound is produced for which the formula $\text{C}_{30}\text{H}_{48}\text{O}_3$ and the name suberonolactone is proposed. An attempt to determine the neutral equivalent of the compound revealed

that it was neutral although the sodium salt had previously been prepared. Thus the substance must contain a COOH group which has reacted with another group in the molecule to form either an anhydride or a lactone. Of the various formulas by which the above properties can be explained the only one which can be reconciled with the analytical results and molecular weight determination is $C_{30}H_{48}O_3$. This compound is formed from friedelin by splitting the ring to form suberic acid and by oxidation of a tertiary hydrogen at some other point in the molecule to hydroxyl. Formula IX can then be written for suberono-lactone.



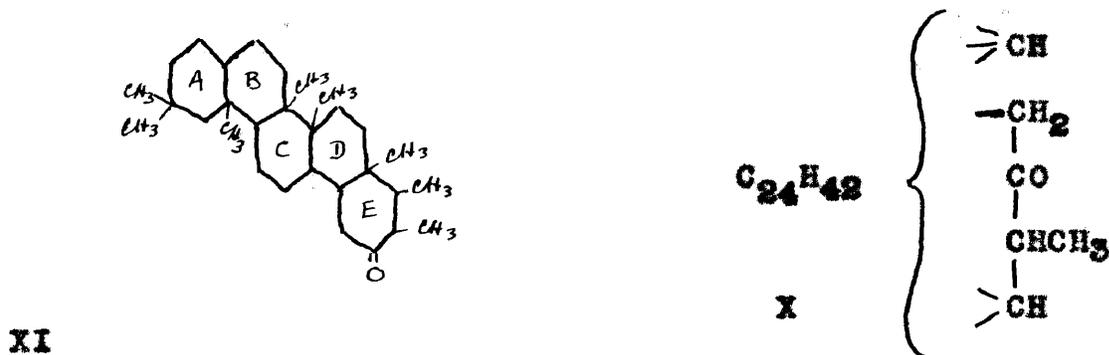
A small amount of suberonolactone is formed when friedelene is oxidized with chromic acid. This action would be expected as a result of the normal splitting of the double bond in friedelene by chromic acid.

The analyses for suberono-lactone check the theory for $C_{30}H_{50}O_3$ more closely than $C_{30}H_{48}O_3$. There is about 0.4 difference in the percents of both carbon and hydrogen

required by these formulas. However, no formula that will explain the properties of suberono-lactone can be devised other than $C_{30}H_{48}O_3$. This same difficulty has been encountered by Ruzicka¹¹ in his work on the oxidation of oxymethelene-allo-betulon.

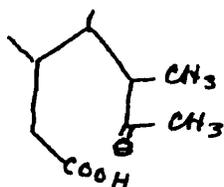
It has been noted that suberonic acid on standing at room temperature in alkaline solution in an organic solvent such as dioxan or ethyl alcohol undergoes a change which is probably stereochemical in nature. The melting point of the acid recovered from these solutions is considerably lower.

The partial formula for friedelin (X) based on the evidence obtained in this research locates tentatively the position of the carbonyl group in the nucleus of the friedelin molecule XI.¹²

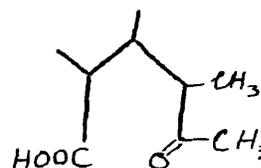


Using only ring E of this formula the structures of some of the compounds prepared during this work are

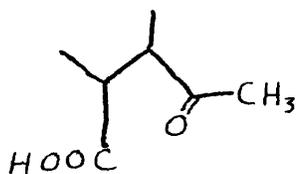
given below:



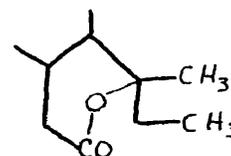
suberic acid



norsuberic acid



C₂₇ keto-acid



suberono-lactone

The carbon atom to which the lactone ring in suberono-lactone is attached is doubtful. However, since oxidation does take place at this point in the formation of the C₂₇ keto acid, the assumption that the ring is attached to that carbon atom is reasonable.

The formation of lactones by both suberolic and norsuberic acids would seem to indicate that ring E of the compound is five membered. If this were true, suberolo-lactone and norsuberolo-lactone would be the normal delta and gamma lactones. However, there is no assurance that the lactone rule will apply equally as well to a system in which the carboxyl group and the hydroxyl group are attached to a condensed ring system. The failure of the Blanc rule¹⁵ under these conditions is noteworthy. In addition epsilon lactones,

the type proposed for suberole-lactone, are not unknown. For example¹⁴ menthone is oxidized to beta methyl epsilon isopropyl epsilon caprolactone, and tetrahydro carvone yields beta isopropyl epsilon methyl epsilon caprolactone. Likewise methyl cyclohexanone can be converted to the lactone of methyl epsilon hydroxy caproic acid. In view of these facts the six member ring as written is reasonable.

PREPARATION AND PURIFICATION OF MATERIALS

The friedelin used in this research was extracted from 20 to 40 mesh cork and purified through the benzoate or phenylacetate by the method described by Drake and Jacobsen.¹

EXPERIMENTAL

Friedelinol: To one gram of friedelin in 100 ml. of boiling n-amyl alcohol was added 2 g. of sodium. After refluxing until all of the sodium had dissolved, the alcohol was removed by distillation with steam and the product was crystallized from benzene - ethyl acetate mixture or from amyl alcohol. The carbinol was obtained in 90% yield in the form of hexagonal plates melting at 301-304°.

Analysis. Calcd. for $C_{30}H_{52}O$: C, 84.03; H, 12.23

Found: C, 83.81, 83.75; H, 12.10, 12.08.¹

Friedelinol has been prepared from crude friedelin by the above method in 50 to 65% yield. This is a higher yield (based on the crude friedelin) than can

1. The author wishes to thank Dr. J. R. Spies for these analyses.

be obtained if the crude is purified through an ester before reduction.

Friedelinyl Iodide: A mixture of 0.5 g. of friedelinol, 0.2 g. of red phosphorus, 1.3 g. of iodine and a small piece of white phosphorus in 60 ml. of dry benzene was refluxed for three hours. The warm solution was shaken with small portions of mercury to remove the iodine and evaporated to 5 ml. in a vacuum. Water was added, the benzene was distilled off in a vacuum, and the product was crystallized from 25 ml. of benzene. One tenth of a gram of substance contaminated with mercuric iodide was obtained. The mercuric iodide was completely removed by rapid leaching of the substance with 2 ml. of benzene. Three recrystallizations from benzene-ethyl acetate mixture produced a product which melted with decomposition at 224-226°.

Analysis. Calcd. for $C_{30}H_{51}I$: I, 23.57.

Found: I, 23.59, 23.36¹

The molecular weights of friedelin calculated from these analyses are 426 and 432. The theory for $C_{30}H_{50}O_2$ is 426.

1. The author wishes to thank Dr. R. P. Jacobsen for these analyses.

Friedelinyl methyl ether: A solution of 0.04 g. of friedelinol in 20 ml. of methyl iodide was refluxed with silver oxide for several hours. The solution was filtered and evaporated. On crystallization from ethyl acetate the product melted at 265 to 267°.

Analysis: Calcd. for $C_{31}H_{54}O$: C, 84.09; H, 12.30.

Found: C, 84.04; H, 12.25.¹

Friedelinyl acetate: One g. of friedelinol was refluxed with 100 ml. of acetic anhydride for two hours. The substance which crystallized on cooling was recrystallized from benzene yielding 0.7 g of long needles melting at 315-316°.

Analysis. 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 2.8 g. of friedelinol in 125 ml. of dry pyridine was added 15 ml. of benzoyl chloride. After refluxing for one half hour, 300 ml. of 95% ethyl alcohol was added and the solution was cooled to room temperature. The resulting precipitate was crystallized from benzene-ethyl alcohol mixture yielding 2.4 g. of long needles which melted at 250-251°.

1. The author wishes to thank Dr. J. H. Spies for this analysis.

Analysis. 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.

Phenylfriedelene: Phenyl magnesium bromide was prepared in ethyl ether from 25 ml. of bromobenzene and 6 g. of magnesium. After the addition of an equal volume of dry benzene, a solution of 5 g. of friedelin in 500 ml. of benzene was added at room temperature. The mixture was refluxed for one half hour. The crude product was obtained by pouring the reaction mixture into dilute acid removing the benzene by steam distillation. Four crystallizations from ethyl acetate yielded 0.3 g of a substance melting constantly at $269-271^{\circ}$.

Analysis. Calcd. for $C_{36}H_{54}$: C, 88.82; H, 11.18.

Found: C, 88.84, 88.97; H, 11.26, 11.30.

The rest of the material from this reaction could not be crystallized and would not react with acetic anhydride to yield a crystalline substance.

Friedelin methylcarbinol: By a method similar to that described in the preparation of phenyl friedelene, 5 g. of friedelin were treated with methyl magnesium iodide. The solid was leached with 250 ml. of boiling ethyl acetate-benzene mixture (2:1), and filtered. The substance which

crystallized from the filtrate was recrystallized several times from benzene to yield a product which melted at 316-319°.

Analysis. Calcd. for $C_{31}H_{54}O$: C, 84.09; H, 12.30.

Found: C, 83.98, 84.19; H, 12.43, 12.42.

From the solid which did not dissolve in the leaching process was isolated by crystallization from benzene a small quantity of methyl friedelene.

Methyl friedelene: One half gram of friedelin methyl carbinol was refluxed with 50 cc of acetic anhydride containing just enough xylene to bring about complete solution. After two hours one half of the solvent was removed by distillation. The product which separated on cooling was crystallized from benzene and ethyl acetate to a constant melting point of 272-274°.

Analysis. Calcd. for $C_{31}H_{52}$: C, 87.65; H, 12.35.

Found: C, 87.65, 87.70; H, 12.36, 12.47.

Friedelene: Five grams of friedelinyl benzoate were heated in an atmosphere of nitrogen at 280-320° for three and one half hours. The benzoic acid was removed by washing with 10% sodium hydroxide. After washing with water the solid was crystallized from ethyl acetate-benzene mixture. Further crystallization from ethyl acetate yielded 3 g. of a

product which melted at 257-258^o. This substance gives a yellow color with tetranitromethane.

Analysis. Calcd. for C₃₀H₅₀: C, 87.72; H, 12.28.

Found: C, 87.89, 87.98; H, 12.37, 12.26.

Attempts to dehydrate Friedelinol directly by the action of sulfuric acid, oxalic acid, sodium bisulfate, phosphorus pentachloride and thionyl chloride resulted in products that could not be crystallized.

Oxidation of friedelene-friedelenone and

norsuberolo-lactone: To a solution of 3.6 g. of friedelene in 900 ml. of acetic acid was added 2.4 g. of chromic anhydride. The solution was stirred at 97^oC for six hours. At the end of this time 500 ml. of water and a little methyl alcohol were added and the mixture was boiled for ten minutes, cooled and filtered. The yield of light green solid was 3.5 g. This was dissolved in ether and shaken with 10% NaOH solution. The ether layer was evaporated until solid started to precipitate, cooled and filtered. One recrystallization of this substance from ether yielded 1 g. of a white crystalline compound which melted at 290-291^o.

Analysis. Calcd. for C₃₀H₄₈O: C, 84.83; H, 11.40.

Found: C, 84.83, 84.83; H, 11.32, 11.36.

Active hydrogen: 0.446 millimol yielded no methane.

The compound gives a yellow color with tetranitromethane.

Acidification of the alkaline extract yielded 1.5 g. of amorphous solid. To this solid, dissolved in 50 ml. of boiling normal propyl alcohol, was added 3 g. of sodium in small pieces. After all of the sodium had dissolved the solution was diluted with 500 ml. water and acidified. The white solid thus obtained was crystallized from ethyl acetate to yield a very small quantity of a substance melting at 287-289°. A mixture of this substance with the norsuberolo-lactone from friedelin (M.P. 289-291°) melted at 288-289°.

Oxidation of Friedelin with CrO₃, Suberonic Acid:

To a boiling suspension of 5 g. of friedelin in 600 ml. of glacial acetic acid, was added 2.4 g. chromic anhydride dissolved in 125 ml. glacial acetic acid, over a period of four hours. The solution was refluxed for eleven hours longer, during which time all of the friedelin dissolved. About two thirds of the solvent was removed by distillation and 500 ml. of water was added to the hot residue. After cooling and filtering the solid was dissolved in ether, filtered and shaken with 10% sodium hydroxide. Sodium salts precipitated in the aqueous layer. The mixture was centrifuged

and after pouring off the ether layer the operation was repeated using a fresh portion of ether. Evaporation of the ether solution yielded 0.8 g. of friedelin and 0.2 g. of resinous residue.

The aqueous layer was made acid to congo red, warmed to coagulate the acids and filtered. Four and one half grams of crude acid was obtained. By crystallization from ethyl alcohol-water and then from 95% ethyl alcohol, 1.3 g. of product which melted at 206-207° was obtained.

Analysis. Calcd. for $C_{30}H_{50}O_3$: C, 78.54; H, 11.00.

Found: C, ~~77.83~~, ~~77.75~~; H, 10.91, 11.02.
av = 78.60

Neutralization Equivalent.

146.7 mg acid required 6.20 ml. of 0.05105 N NaOH.

157.9 mg. acid required 6.70 ml. of 0.5105 N NaOH.

Calcd. for $C_{30}H_{50}O_3$: 458. Found: 463, 461.

The neutralization equivalents were run in ethyl alcohol solution using 0.05 N NaOH and phenolphthalein. The alcohol used was distilled from sodium hydroxide.

Methyl suberate: This compound was prepared from the crude acid fraction obtained by oxidation of friedelin. Two grams of the acid was dissolved in absolute ethyl alcohol containing 0.1 g of dissolved sodium, and 10 ml. of

methyl iodide. After refluxing for three hours, about two thirds of the solvent was evaporated, and the residue was poured into water. This mixture was extracted with ether. The ether layer was washed with a little sodium bisulfite solution and evaporated. Several crystallizations from methyl alcohol produced a substance which crystallized in long needles and melted at 249-251°.

Analysis. 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.

Saponification equivalent.

27.04 mg. ester equivalent to 1.05 ml. of 0.0544 NH_2SO_4 .

47.79 mg. ester equivalent to 1.87 ml. of 0.0544 NH_2SO_4 .

Calcd. for $C_{31}H_{52}O_3$: 472 Found: 473, 471.

Saponification equivalents were determined by the method described by Drake and Jacobsen.¹

Suberolo-lactone and norsuberolo-lactone: To a boiling solution of 2.45 g. of the lower melting crude acid fraction obtained from the oxidation of friedelin, in 140 ml. of normal propyl alcohol, 6 g of sodium was added in small pieces. After cooling the mixture was diluted with 500 ml. of water, made acid to congo with hydrochloric acid and filtered. The solid was dissolved in 160 ml. of boiling ethyl alcohol, cooled and filtered. The solid, thus obtained was crystallized from ethyl acetate three times to yield a substance melting

at 309-312°.

Analysis. 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 ethyl alcohol filtrate was evaporated to about half its volume, cooled and filtered. This solid was crystallized from ethyl acetate to a constant melting point of 289-291°. A mixed melting point with suberolactone showed the normal depression.

Analysis. Calcd. for $C_{29}H_{48}O_2$: C, 81.24; H, 11.30.

Found: C, 81.09, 81.29; H, 11.29, 11.34.

Saponification Equivalent.

45.28 mg. lactone equivalent to 1.93 ml. of 0.0544 N

H_2SO_4 .

48.39 mg. lactone equivalent to 2.07 ml. of 0.0544 N

H_2SO_4 .

Calcd. for $C_{29}H_{48}O_2$: 428. Found: 431, 429.

C₂₇ ketoacid: The crude acid from oxidation of friedelin from which all of the suberonic acid had been removed by crystallization was dissolved in ethyl alcohol. Part of the substance was precipitated as sodium salt by addition of 10% potassium hydroxide. The precipitate was filtered and converted to acid (1.1 g) by treatment with hydrochloric acid. The solid was dissolved in aqueous alcohol

and cooled. The liquid was poured off from the oil which separated, diluted with water and acidified. This treatment was repeated twice more. The product finally obtained melted at 121-124° to a very viscous clear liquid.

Analysis. Calcd. for $C_{26}H_{42}O_3$: C, 77.53; H, 10.54.

Calcd. for $C_{27}H_{44}O_3$: C, 77.81; H, 10.66.

Found: C, 77.62, 77.44; H, 10.67, 10.62.

Neutral equivalent.

80.7 mg of acid required 3.81 ml. of 0.05105 N NaOH.

57.2 mg. of acid required 2.73 ml. of 0.05105 N NaOH.

Calcd. for $C_{26}H_{42}O_3$: 402. Calcd. for $C_{27}H_{44}O_3$: 416.

Found. 415, 411.

Suberono-lactone.a): To a boiling solution of 5 g. of friedelin in 500 ml. of glacial acetic acid was added 10 g. chromic oxide over a period of four hours. After refluxing the solution for seventeen hours longer, half of the acetic acid was distilled off and water was added. The product obtained by filtering this mixture was dissolved in ether and shaken with 10% sodium hydroxide solution. The solid sodium salt which precipitated in the aqueous layer was filtered off, dissolved in dilute alcohol and acidified. The solid thus obtained was dissolved in ethyl alcohol and the solution was filtered. The oil which separated on cooling

this solution was dissolved in ethyl alcohol. Water was added to incipient precipitation and then enough 10% sodium hydroxide to precipitate about half of the acid as sodium salt. The solid obtained by acidification of this salt was crystallized from ethyl alcohol to a constant melting point of 127° .

Analysis. Calcd. for $C_{30}H_{48}O_3$: C, 78.88; H, 10.61.

Calcd. for $C_{30}H_{50}O_3$: C, 78.54; H, 11.00.

Found: C, 78.47, 78.22; H, 11.11, 11.00

Saponification equivalent.

105.8 mg. lactone equivalent to 4.12 ml. of 0.0544 N H_2SO_4 .

Calcd. for $C_{30}H_{48}O_3$: 456. Found: 437.

b) The solid sodium salt, obtained when the crude oxidation product of friedelene is dissolved in ether and shaken with alkali, was separated and washed with ether. Treatment with hydrochloric acid produced the solid acid. This substance on crystallization from ethyl alcohol yielded a product melting at 127° . A mixed melting point of this product with the suberono-lactone obtained from friedelin showed no depression.

Analysis. Calcd. for $C_{30}H_{48}O_3$: C, 78.88; H, 10.61.

Found: C, 78.42, 78.76; H, 11.12, 11.07.

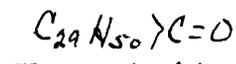
Discrepancies in analyses and saponification equivalent are due to impurities. A small amount of insoluble material was noted in the saponification reaction mixture.

SUMMARY

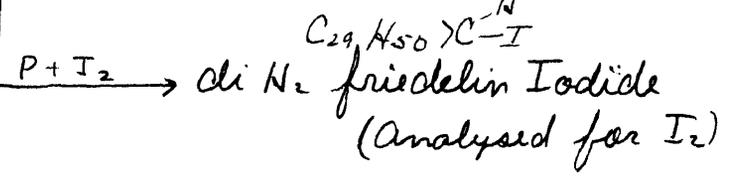
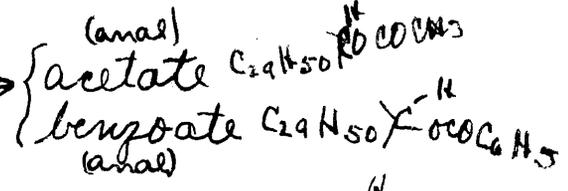
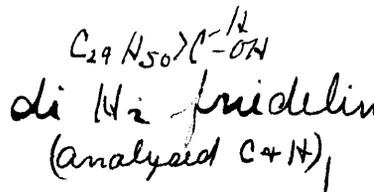
1. Friedelin has been reduced to a secondary alcohol, friedelinol, which was characterized by the formation of an acetate, a benzoate, a methyl ether and an iodide.
2. Friedelin methyl carbinol and the unsaturated hydrocarbons, methyl friedelene, phenyl friedelene, and friedelene have been prepared.
3. Friedelene has been oxidized to friedelenone, norsuberonic acid, and suberono-lactone.
4. Friedelin has been oxidized to suberonic acid, norsuberonic acid, suberono-lactone, and a C₂₇ keto acid.
5. A partial formula for friedelin has been proposed, locating six of the carbon atoms in the molecule.
7. The position of the carbonyl group in the friedelin nucleus has been tentatively located.

REFERENCES

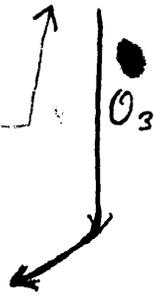
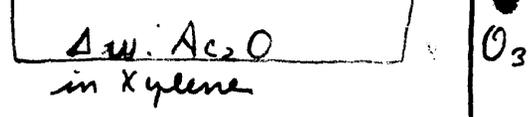
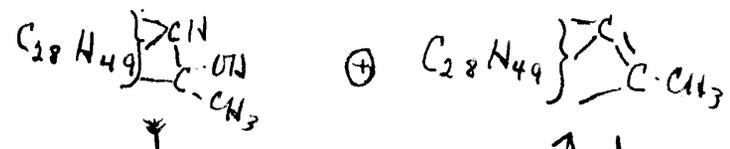
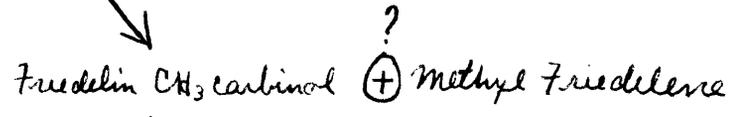
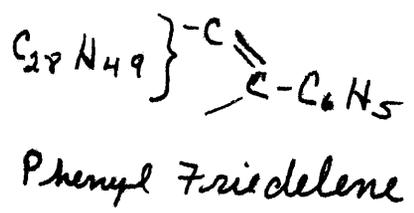
1. J. A. C. S. 57, 1570 (1935).
2. J. A. C. S. 57, 1854 (1935).
3. B. 47, 1143 (1914).
4. B. 46, 1178 (1913).
5. B. 47, 2624 (1914).
6. B. 53, 488 (1920).
7. C. 1908 I 1295.
8. Z. 1871, 4; B. 7, 1363.
9. Beilstein, Vol. II p. 353.
10. Ruzicka - Helv. Chim. Acta. 17, 429 (1934).
11. Ruzicka - Helv. Chim. Acta. 17, 426 (1934).
12. W. T. Haskins - Thesis, U. of Md. (1936).
13. Wieland & Dane - Z. physiol. chem. 210, 268 (1932).
14. Richter - Anschütz Vol. I p. 471 (12th edition).



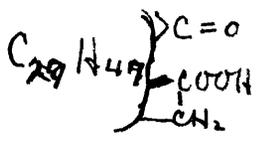
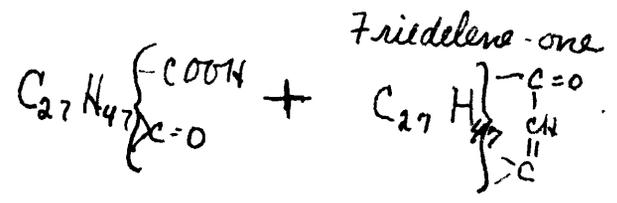
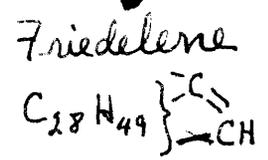
Friedelin $\xrightarrow[alc.]{Na}$



$C_{29}H_{50}$ in
 H₂O
 B.P. 160°



280°-320°
 in ~~the~~ N₂
 $-C_6H_5COOH$



$-C_4H_8$

