

**The Isolation of Friedelin and Cerin from Cork**  
**and**  
**A Study of the Properties and Molecular Weight of Friedelin**

by

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## HISTORY AND INTRODUCTION

Cork, being an exceedingly complex material, has been for more than a century the subject for the study of a large number of chemical investigations.

To Chevreul<sup>1</sup> belongs perhaps the credit for the discovery of those particular compounds habitually referred to in the chemical literature as the cork alcohols. He describes the isolation of a material, obtained by the extraction of ground cork with alcohol, which he thought to be a single pure substance. He named it "cerine" because it resembled a wax. However, it did not possess a low melting point, was less soluble in alcohol than a wax and furthermore the filtrate from the water treatment of an alcoholic solution of the substance showed no acidity to litmus. It remained unaltered on treatment with hot alcoholic potassium hydroxide and was decomposed by hot nitric acid to give oxalic acid. Although he reported no analyses or melting point, Chevreul concluded that the material was not a wax. Boussingault<sup>2</sup> later obtained a similar material by extracting cork with ether. The brown resinous solid left upon evaporation of the ether, apparently without being further carefully purified, gave analyses

which corresponded to the formula  $C_{32}H_{20}O$ .

The following analytical results obtained for a colorless crystalline material from cork were reported by Doeping<sup>3</sup>: C, 75.63, 75.52; H, 10.55, 10.49. From these values he concluded the formula to be  $C_{28}H_{20}O_3$ . This formula was further modified by Siewart<sup>4</sup> who proposed  $C_{17}H_{28}O$  as best fitting the mean of eight analyses (C, 82.30; H, 11.39) which he obtained for a material extracted from cork with alcohol and for which he proposed the name phellyl alcohol.

Kügler<sup>5</sup> observed that the exhaustive extraction of 200 grams of ground cork with chloroform in a sealed tube at  $100^{\circ}$  yielded 20 grams of a solid material from which, by recrystallization from absolute alcohol, he obtained an amorphous substance melting at  $126^{\circ}$  and one that crystallized in needles melting at  $238^{\circ}$ . He recorded the solubility of the crystalline material in various solvents as shown in Table I. Kügler proposed for cerin the formula  $C_{20}H_{22}O$ . In a paper published somewhat later, Thoms<sup>6</sup> describes the extraction of 10 kilograms of ground cork with ether. The extract, upon removal of the ether, yielded 475 grams of a dry, although somewhat pasty, brown mass. This crude material was leached with cold ether in two

Table I. Solubility of the crystalline product obtained by Kugler.

G. per 100 g. solvent.

CHCl <sub>3</sub>		C <sub>6</sub> H <sub>6</sub>		Pet. Eth.		99% C <sub>2</sub> H <sub>5</sub> OH	
Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold
3.8	2.6	1.2	1.0	1.6	1.0	0.37	0.11

main portions after which the remaining residue was boiled with 5% sodium carbonate solution and then with 5% potassium hydroxide. Following this treatment, the insoluble matter was filtered off, washed with water and dried. Upon recrystallization from ethyl acetate the substance melted at 249° and gave the following series of analyses:

Subs.	G. H <sub>2</sub> O	G. CO <sub>2</sub>	%C	%H
0.1234	0.1265	0.3683	81.40	11.39
.1312	.1380	.3914	81.36	11.68
.1667	.1726	.5009	81.94	11.50
.1554	.1635	.4663	81.83	11.69
.1338	.1390	.3998	81.50	11.54

Formulas fitting these values are C<sub>30</sub>H<sub>50</sub>O<sub>2</sub> (C, 81.38; H, 11.39) and C<sub>32</sub>H<sub>54</sub>O<sub>2</sub> (C, 81.72; H, 11.48). Thoms states he was able to prepare an acetyl and a benzoyl derivative, although he does not describe them further. Believing cerin might be related to the plant sterols, he made two color tests on his product. The first, with acetic anhydride and concentrated sulfuric acid, gave a rose red color and the second, with concentrated sulfuric acid and a

chloroform solution of the substance, he describes as giving a yellow color, which, after several hours standing, became violet.

The important fact that this crystalline material from cork really consisted of two substances which could be separated from each other by a series of recrystallizations from chloroform and which differed markedly in both their solubility in chloroform and percentage composition, was demonstrated by Istrati and Ostrogoovich<sup>7</sup>. Friedel<sup>8</sup>, in a note to Istrati, had called the attention of the latter to the fact that Chevreul had previously isolated cerin, adding that he himself had observed that the substance melted at 248°, was soluble in both ethyl alcohol and chloroform, gave analyses corresponding to the formula  $C_{12}H_{17}O$  and appeared on further study to contain a carbonyl function. In honor of Friedel, Istrati called the more soluble of the two compounds, friedelin. These workers refluxed the crude extracted material with alcohol, filtered off the insoluble matter and washed it with moderately warm alcohol. The part insoluble in the warm alcohol was extracted in a Soxhlet apparatus leaving in the thimble a quantity of brown resinous material. The cooled filtrate was then filtered

to yield impure cerin which was further purified by several recrystallizations from chloroform to give long silky needles melting at  $234-4.5^{\circ}$ . From the filtrates, crude friedelin melting at  $250^{\circ}$ , was obtained. This was decolorized with charcoal in benzene solution and then partially extracted in a Soxhlet apparatus with chloroform. By repeating this operation several times there was obtained a product melting constantly at  $263-3.5^{\circ}$ , which crystallized from alcohol in perfectly white brilliant flat needles. The solubilities of the two compounds in chloroform and absolute alcohol were given as follows:

Table II. Solubility of Cerin and Friedelin according to Istrati.

	G. per 100 cc. solvent.			
	CHCl <sub>3</sub>		99% C <sub>2</sub> H <sub>5</sub> OH	
	23°	Boiling	26°	Boiling
Cerin	0.33	1.1	0.073	0.23
Friedelin	11.5	28.5	0.050(21°)	0.37

Analysis of cerin gave the values, C, 80.86, 80.85, 80.75; H, 11.47, 11.30, 11.50, which according to Istrati, corresponded to the formula  $C_{27}H_{44}O_2$  (C, 81.00; H, 11.00) with a molecular weight of 400. One determination of the molecular weight by the ebulliscopic method gave 400.7. In the case of friedelin the analyses were C, 83.52, 83.40,

83.36; H, 11.68, 11.56, 11.61, corresponding either to  $C_{21}H_{34}O$  (C, 83.44; H, 11.26) with a molecular weight of 302 or to  $C_{43}H_{70}O_2$  (C, 83.49; H, 11.34) with a molecular weight of 618. They found a molecular weight of 645.

Both substances were found to be optically active, the specific rotation in chloroform changing with the concentration to give the maxima, for cerin in a solution containing 0.3306 gram percent,  $(\alpha_D)^{26} -84.69^\circ$  and for friedelin in a solution containing 0.8210 gram percent,  $(\alpha_D)^{26} -48.72^\circ$ .

In carrying out the two color tests described by Thoms, these workers found that both substances in acetic anhydride solution gave a red color with fuming sulfuric but only a faint color with concentrated sulfuric acid. The chloroform solutions in both cases when agitated with concentrated sulfuric acid failed to give a violet color.

The chemical literature contains no further record of investigation into the question of the chemical constitution of friedelin and cerin.

Scurti<sup>2</sup>, in recording the findings of some studies of the formation of fats in oleaginous plants, has made the statement that the compound which earlier investigators called cerin, is in reality identical with the so-called cerose alcohols, "oleanol" (olive), ligustrol (Japanese privet), and fillirol (*phillyrea media*) having the formula  $C_{31}H_{50}O_2$ .

From the work of van der Haar<sup>10</sup> and others it is now apparent that "oleanol" is a hydroxy acid and not a trihydroxy compound as was first supposed. The name given to this compound by van der Haar and the one now accepted in the chemical literature is oleanolic acid.

Winterstein<sup>11</sup> classifies cerin among the sapogenins as a dihydroxy triterpenoid. A close examination of the literature concerning these substances reveals several compounds related to the triterpenes and sterols containing thirty carbon atoms. A casual examination of the following table of such compounds and their derivatives will serve to show that cerin and friedelin are among the very few which exhibit a laevo-rotation.

Table III. Physical constants of some alcohols, oxides and ketones of the empirical formula  $C_{30}H_{48-52}O_{1-2}$

Form.	Subs.	( $\alpha$ ) <sub>D</sub> CHCl <sub>3</sub>	M.p.	Derivatives.
$C_{30}H_{48}O$				
$\alpha$ -Amyrone <sup>12-14, 16</sup>	--	--	124-6°	Oxime 236.5° (234°); Hydrazone 252°; Enolbenzoate 197-8°; Bromo-190°.
$\beta$ -Amyrone <sup>13-15</sup>	--	--	177-9°	Bromo- 198-9°; Enolbenzoate 181-2°; Oxime 265-7°.
Apobetulins <sup>16, 19</sup> ( $\beta$ -Alloapobetulin)	-28.69°	186-7°		Acetate 203-4° $\alpha_D$ -44.38°.
Apoallobetulin <sup>17</sup>	74.78°	198-201°	--	
$\gamma$ -Apoallobetulin <sup>18</sup>	--	242-3°	--	

Table III (continued)

Form.	Subs.	( $\alpha$ ) <sub>D</sub> CHCl <sub>3</sub>	M.p.	Derivatives.
Lupeone <sup>20-22</sup>		63.1° (57.3°)	170-2°	Dibromo- 248-54°; Oxime 267-78.5° (274°) $\alpha_D$ 20.5° (12-26°).
Agnoosterol <sup>23</sup>		70.5°	162°	Acetate 173-4° $\alpha_D$ 90.4°; Benzoate 203° $\alpha_D$ 103.2°.
Lanostenone <sup>24</sup>		71.9°	116.5°	--
Oleanone <sup>13</sup>		95.8°	168-72°	--
<b>C<sub>30</sub>H<sub>48</sub>O<sub>2</sub></b>				
$\beta$ -Amyrone				
oxide I <sup>14</sup>		143°	237°	--
$\beta$ -Amyrone				
oxide II <sup>14</sup>		--	234°	--
$\beta$ -Amyrone				
oxide III <sup>14</sup>		125°	183°	--
Hydroxy -				
amyrone <sup>15</sup>		--	216-7°	Oxime 248-51°.
$\beta$ -Amyrilene				
dioxide <sup>18</sup>		--	199-201°	--
$\alpha$ -Amyrone				
oxide <sup>14</sup>		141°	193°	--
Betulone <sup>19, 20</sup>		19.97°	207-8°	Enolacetate 182-3° $\alpha_D$ 30.26°.
Allobetulone <sup>19, 26-28</sup>		84.40°	230-1°	Enolbenzoate 228-30° $\alpha_D$ 33.16°; Oxime 285-90°; Dibromo- 220° $\alpha_D$ 34.75°; Phenylhydrazone 223°.
Mudarol <sup>29</sup>		--	176°	Acetate 195-6°.
Serposterol <sup>30</sup>		-68.5°	159-60°	--
<b>C<sub>30</sub>H<sub>50</sub>O</b>				
Friedelin	$\alpha_{5+6}$	-29.4°	255-61°	Enolbenzoate 255-62° $\alpha_{24}$ 66.2°.
Dihydro- $\beta$ -				
amyrilene oxide <sup>18</sup>		--	126-7°	--
$\alpha$ -Amyrin <sup>31, 32, 19, 21</sup>		82.5° (91.6° C <sub>6</sub> H <sub>6</sub> )	181-6°	Acetate 220-5° $\alpha_D$ 77.9° (75.5°); Benzoate 191-4°

Table III (continued)

Form.	Subs.	( $\alpha$ ) <sub>D</sub> CHCl <sub>3</sub>	M.p.	Derivatives.
$\alpha$ -Amyrin (continued)				
$\beta$ -Amyrin	<sup>21, 22, 23, 24</sup> <sup>21</sup>	88.4° (98.1° C <sub>6</sub> H <sub>6</sub> )	193-7°	(benzoate) $\alpha_D$ 94.57°; Bromo- 178-9°; Acetate 235-41° $\alpha_D$ 81.2°; Benzoate 229-35° $\alpha_D$ 100.2°; Dibromo- 210-6°.
$\gamma$ -Amyrin	<sup>16</sup>	42.0°	168-9°	--
Oleanol	<sup>11a</sup>	59.1°	216-20°	Acetate 209-10° $\alpha_D$ 44.7°.
Lupeol	<sup>21, 22, 23, 24</sup> <sup>46</sup>	27.5° (24.57°)	211-8°	Acetate 214-8° $\alpha_D$ 43.33° (41.23°); Benzoate 270-4° $\alpha_D$ 60.4°; Bromo- 185° $\alpha_D$ 3.8°; Dibromo- 210-6° $\alpha_D$ 25.0°.
$\alpha$ -Allo- lupeol	<sup>35</sup>	--	191°	Acetate 199° $\alpha_D$ 45.46°; Benzoate 256° $\alpha_D$ 42.82°.
$\beta$ -Allo- lupeol	<sup>35</sup>	--	151°	Acetate 196° $\alpha_D$ 28.57°; Benzoate 228°.
Alnulin	<sup>39</sup>	--	126°	Acetate 237°; Bromo- 210°.
$\alpha$ -Lactu- cerol	<sup>40</sup>	78.44°	203°	Benzoate 257°.
$\beta$ -Lactu- cerol	<sup>40</sup>	53.8°	165°	Benzoate 260°
Lanosterol	<sup>23, 24</sup>	58.0°	140-1°	Acetate 113-4° $\alpha_D$ 55.2°; Benzoate 191.5° $\alpha_D$ 74.5°.
Lanosterol A	<sup>24</sup>	58.7°	142.5-3.5°	Acetate 126-7° $\alpha_D$ 59.4°.
$\alpha$ -Dihydro- agnosterol	<sup>23</sup>	60.9°	147-8°	Acetate 162-3° $\alpha_D$ 84.4°.
$\beta$ -Dihydro- agnosterol	<sup>23</sup>	36.6°	141-2°	Acetate 133° 48.9°.
C <sub>30</sub> H <sub>50</sub> O <sub>2</sub>				
Cerin	$\alpha_{5+6}$	-43.5°	247-51°	--
$\alpha$ -Amyrin oxide	<sup>14</sup>	--	193°	--
$\beta$ -Amyrin oxide	<sup>14, 15, 18</sup>	--	201-4°	Acetate 291-3°.
( $\beta$ -Amyrin dioxide)				
(Hydroxy- $\beta$ -amyrin)				

Table III (continued)

Form.	Subs.	$(\alpha)_D$ CHCl <sub>3</sub>	M.p.	Derivatives.
Dihydro- betulone <sup>19</sup>		10.43°	180-2°	--
Hederabetulin <sup>11</sup>		56.1°	276-8°	Diacetate 190° $\alpha_D$ 68.6°
Betulin <sup>17-19</sup> <del>17-18</del>		19.96° (C <sub>5</sub> H <sub>5</sub> N)	251-5°	Diacetate 219-20° $\alpha_D$ 21.99°; Dibenzoate 145-7° (181°) $\alpha_D$ 43.28°.
Allobetulin <sup>17-19</sup> <del>25-27</del>		48.25°	259-65°	Bromo- 215° Acetate 275-6° $\alpha_D$ 54.61°; Benzoate 275-6° $\alpha_D$ 70.26°.
Heterobetulin <sup>27</sup>		11.59°	267-8°	Diacetate 248-9° $\alpha_D$ 28.29°; Dibenzoate 222-8° $\alpha_D$ 35.49°.
Brein <sup>19</sup> <sup>41, 43</sup>		65.5°	215-9°	Diacetate 196°; Di- benzoate 209-10°.
Arnidiol <sup>43</sup>		62.8° (CH <sub>3</sub> ) <sub>2</sub> CO	249-50°	$\alpha$ -Diacetate 181-3°; $\beta$ - " 100-1°.
Paradiol <sup>44</sup>		41.0° (45.0° (CH <sub>3</sub> ) <sub>2</sub> CO)	238°	Diacetate 140-5° $\alpha_D$ 63.6°.
C <sub>30</sub> H <sub>52</sub> O				
$\alpha$ -Dihydro- lanosterol <sup>23, 24</sup>		51.9°	149-50° (143°)	Acetate 118-20° $\alpha_D$ 52.9°.
Dihydrolupeol <sup>28</sup>		-17.5° (-16.19°)	201-2°	--
C <sub>30</sub> H <sub>52</sub> O (No name)		--	251°	Acetate 237°.
C <sub>30</sub> H <sub>52</sub> O <sub>2</sub>				
Dihydrobetulin <sup>19</sup>		-19.14° (-22.0° C <sub>5</sub> H <sub>5</sub> N)	277°	Diacetate 253-5° $\alpha_D$ -6.50°.
Dihydro- hederabetulin <sup>11</sup>		17.7°	235-9°	Diacetate 131-2° $\alpha_D$ 42.2°.

As a result of some recent unpublished observations concerning friedelin and cerin made by Cooke in this laboratory it became apparent, both on the basis of melting points and percentage composition, that the early workers, with the probable exception of Thoms, who undoubtedly had succeeded in obtaining pure cerin, had not isolated perfectly homogeneous compounds. By several recrystallizations from chloroform, Cooke obtained cerin melting at  $247-8^{\circ}$  which gave the following analytical values:

C	-	-	-	81.41, 81.41, 81.90
H	-	-	-	12.08, 11.66, 11.88

The friedelin obtained in this manner melted at  $262.5-3^{\circ}$  and gave upon analysis;

C	-	-	-	84.42, 84.50, 83.81
H	-	-	-	12.05, 12.26, 12.17

He further reported that the two compounds when refluxed with acetic anhydride containing a little concentrated sulfuric acid yielded the same acetate, the identity being established by analysis and saponification values;

Acetylated friedelin

Acetylated cerin

C	-	-	82.64, 82.64	-	-	-	82.82, 82.91
H	-	-	11.57, 11.26	-	-	-	11.68, 11.70
Mol. Wt. 449.8				Mol. Wt. 454.0			

That neither of these products is identical with friedelin acetate, has been shown by Shrader<sup>48</sup>.

The investigation herein described was undertaken with the aim of studying the properties of friedelin and cerin as a primary step in a further study of the chemical constitution of these compounds.

### EXTRACTION

Upon the recommendation and following the practice of Cooke, ethyl acetate was chosen as the extraction solvent. The commercial product of 99% purity manufactured by the U. S. Industrial Chemical Co. was found suitable. The cork powder used in the preliminary trial extractions and the 20-30 mesh ground cork used in all subsequent extractions as a source of friedelin and cerin was supplied through the courtesy of the Armstreng Cork Co., Lancaster, Pennsylvania.

For an initial series of trial extractions a percolator type apparatus designed and built by Drake and Spies<sup>47</sup> was employed. Using cork powder, a charge of about two pounds yielded upon extraction 1.5% its weight of a brown colored solid material. Difficulty was immediately encountered in the extraction process due to the very poor porosity of the cork powder. Moreover, the extract was dark reddish-brown in color and the solid material obtainable from it was seriously contaminated with brown colloidal matter. When the charge was changed to a fifty-fifty mixture of powder and 20-30 mesh ground cork, the porosity of the mass improved but the solid product was still quite dark colored. With 20-30 mesh ground cork alone, the ex-

tract was light orange-brown in color even after twenty hours percolation and the solid material separating from it appeared nearly white. Due to the bulkiness of the ground cork a charge of only about 500-700 grams could be extracted each time, so it was thought advisable to carry out the process on a much larger scale.

Through the courtesy of the Bureau of Chemistry and Soils of the U. S. Department of Agriculture there was obtained an extraction apparatus consisting of two kettles fitted with riveted steam jackets and suspended, by means of pivots riveted to the sides of each, on a heavy steel frame so that they could be tipped for discharging. The kettles, being 37" deep with an internal diameter of 15" at the top and 10" at the bottom could be charged, when about two-thirds filled, with five pounds of ground cork. Both jackets were fitted with  $\frac{1}{4}$ " steam connections and the covers with  $\frac{1}{2}$ " vapor outlet pipes in such a manner that one kettle could be used for hot extraction while the other served as a solvent recovery still. The lead-lined copper covers were made vapor tight by using  $\frac{1}{4}$ " by  $1\frac{1}{2}$ " rubber gaskets 18" in outside diameter and were held in place by six or eight 4" standard steel clamps.

The vapor line led from the covers in series to a straight condenser, 45" long and constructed of 10 mm. standard copper tubing with a glass water jacket, inclined downward to make connection with a secondary condenser of similar tubing wound in the form of a spiral and cooled by circulating water in a five gallon crock. With such a condensing system the ethyl acetate could be distilled without appreciable loss at a rate greater than five gallons per hour. The bottom of the extraction kettle was fitted with a round perforated disk of lead covered with copper gauze to support the charge. The steam inlet and vapor outlet of this kettle were made through pipe unions so that the extractor could be made to swing free on its pivots during the discharging operation.

In the typical extraction procedure the extractor was charged with five pounds of ground cork, the cover clamped in place and 17-20 gallons of solvent pumped through the top by means of a simple blower arrangement. The kettle was heated so that 2-3 gallons of solvent was distilled over during a period of about 1-2 hours. The steam was then shut off and, after allowing the kettle to cool somewhat, a small stopcock in the cover was opened and the warm extract drawn off through a  $1\frac{1}{2}$ " brass stopcock at the bottom. The warm extract (about 10 gallons) was then

blown into the recovery still and concentrated to 7-10 liters. During this interval the extractor was charged with an additional 10 gallons of solvent for the second extraction of the same cork charge. The concentrated extract in the recovery still was drawn off slowly while still boiling, filtered and collected in a 12 liter flask to cool. The crystalline material was filtered off and washed with a quantity of ethyl acetate to yield 10-20 grams of dry, nearly white needles. The filtrate was put back into the solvent recovery still with the second extract for further concentration. These filtrates became quite dark colored after four extractions (two charges of cork), and so after every fourth crop had been filtered off, were reserved for final concentration. Each cork charge, after being twice extracted in the manner described, was removed by tipping the extractor and expressed in a cider press to recover an additional 10-15 liters of solvent. This very uneconomical method of recovering the ethyl acetate from the wet cork was used since no facilities for steaming so large an amount of the extracted cork were available. The loss per charge was about 2 gallons.

## PURIFICATION

The great difference in the solubility of friedelin and cerin in chloroform observed by Istrati and Ostrogo-  
vich would lead one at once to consider the recrystalliza-  
tion of the crude extracted solid from this solvent as a  
means of effecting the separation of the two compounds.

The process was carried out by dissolving 25-30<sup>a</sup>  
grams of the crude in the minimum quantity of boiling  
chloroform under reflux, filtering the hot solution and  
cooling. The solid separating from this solution, to-  
gether with an additional small quantity of the less sol-  
uble material obtained by concentration of the chloroform  
solution to about one half its original volume, was fil-  
tered off and recrystallized from chloroform. The crys-  
talline material obtained in this second treatment was  
nearly free of friedelin but contained a small amount of  
brown colloidal matter, the removal of which was complete-  
ly accomplished by recrystallization from benzene. The  
material thus obtained gave a rotation in chloroform sol-

-----

<sup>a</sup>The quantity of material employed need only be an amount  
convenient to manipulate.

ution of  $(\alpha)_{5461}^{22} - 43.3^\circ$  (c=0.300).<sup>b</sup> Further recrystallization from chloroform did not greatly alter the material, the rotation changing only within the precision of the determination for such dilute solutions to give  $(\alpha)_{5461}^{25} - 44.5^\circ$  (c=0.954) and after further recrystallization,  $(\alpha)_{5461}^{27} - 42.4^\circ$  (c=1.18). Cerin obtained in this manner crystallized from chloroform or benzene in silky needles melting with apparent decomposition at  $247-51^{00}$ . The amount of cerin obtainable was 5-10% the total weight of the crude extracted material.

The friedelin, which makes up the bulk of the crude, together with some of the brown colored matter, remains dissolved in the above chloroform filtrate.<sup>c</sup> These were concentrated until solid began to separate from the hot solution, whereupon the addition of an equal volume of acetone to the warm sludge precipitated crude friedelin in the form of a white crystalline powder. The small amount of brown color which remained could then be removed from this solid if necessary by leaching it with hot acetone in which the friedelin is only very sparingly soluble.

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<sup>b</sup> It is unnecessary to pre-treat the crude with 1% KOH in 80% EtOH. The above rotations were determined for cerin from alkali treated crude, while that from untreated was  $(\alpha)_{5461}^{24} - 43.7^\circ$  (c=1.19).

<sup>c</sup> All melting points were made with a calibrated thermometer and are corrected for emergent stem.

Pure friedelin was obtained from this "friedelin rich" material by conversion to an ester and subsequent saponification.

Sublimation in vacuo was used in many cases as a means for the final purification of samples for analysis. The apparatus used consisted of a sublimation chamber constructed of two sections, one 10 cm. and the other 20 cm. long, of 50 mm. pyrex tubing each sealed on one end. The open ends were fitted with brass collars sealed to the glass with "Picein". The contacting surfaces of the brass collars were machined to a plane so that with the aid of a thin film of Lubri-Seal a vacuum tight connection between the two sections was possible. The longer bottom section served to hold the material to be sublimed. In the top section was sealed a condenser of 25 mm. pyrex tubing 34 cm. in length through which cold water could be circulated, and which, when the apparatus was assembled, extended to within 5.5 cm. of the bottom of the sublimation chamber. The latter was evacuated through a side outlet in the upper section leading through a trap immersed in a cooling mixture to a mercury vapor pump backed by an oil pump. The sublimation chamber was heated by means of an electric furnace, the temperature of which was followed by means of

an ordinary 360° thermometer. The charge of material to be successfully sublimed was not to exceed two grams. After partial sublimation had taken place the sublimate could be chipped off of the cold tube and the process continued. The time required for the sublimation of 1.0 to 1.5 grams of material was, depending upon the temperature employed, 20-60 hours.

## DISCUSSION

Cerin, purified by recrystallization from chloroform could be sublimed in vacuo without change in composition at a temperature of  $210-300^{\circ}\text{a}$ . The carbon and hydrogen values obtained upon the combustion of this sublimed material correspond to those calculated for  $\text{C}_{30}\text{H}_{50}\text{O}_2$ , the formula first proposed by Thoms.

Dr. S. B. Hendricks of the Fixed Nitrogen Laboratory of the U. S. Department of Agriculture very kindly consented to measure the refractive indices of both friedelin and cerin. The data he obtained upon the examination of cerin was:

Habit: Narrow laths; nearly needle like.

Extinction: Parallel elongation.

$\text{Ex}_a$ : Character positive, angle less than friedelin and perpendicular to the same face.

Indices of refraction:  $\alpha = 1.550$ ,  $\beta = 1.580$ ,  $\gamma = 1.615$ .<sup>b</sup>  
( $\text{Ex}_a$  figure centered)

Cerin, treated with dry HCl in chloroform solution at  $15-20^{\circ}$  gave a halogen containing derivative which was very soluble in all the usual solvents and isolatable only as a colorless sticky resin or an amorphous solid. It was

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<sup>a</sup>This is the temperature in the furnace outside the sublimation chamber. The temperature in the material being sublimed is perhaps  $20-30^{\circ}$  Lower.

<sup>b</sup>White light.

impossible to obtain a perfectly pure monochloro derivative from this resin due probably to the very labile character of the chlorine atom in the cerin molecule. The material separates from 1:1 ether-absolute alcohol mixture as a white amorphous solid melting at 196-201° with the rapid evolution of HCl.

"Friedelin rich" material treated with benzoyl chloride formed an ester, the reaction proceeding smoothly at a temperature between 150-35° to give a solid product, which upon recrystallization from benzene-ethyl acetate mixture, appeared in the form of flat needles or leaves melting at 255-62°. This material upon sublimation in vacuo showed no change in melting point. Friedelin benzoate is dextro-rotatory, the value in chloroform being  $(\alpha)_{546.1}^{25} 66.2^{\circ}$  ( $c = 1.804$ ). The ester may be saponified in pyridine with alcoholic sodium hydroxide, in benzene-ethyl alcohol mixture with sodium ethylate, or with sodium n-propylate in n-propyl alcohol. The latter method is best for the purification of friedelin since it crystallizes well from this solvent.

Friedelin may be esterified in a similar manner with phenylacetyl chloride,  $\beta$ -phenylpropionyl chloride, and p-iodobenzoyl chloride. The former, being a more vigorous

acylating agent than benzoyl chloride, was used extensively for the purification of friedelin.

Friedelin phenylacetate crystallized from benzene-ethyl acetate in short heavy needles which melted without apparent decomposition at  $244-51^{\circ}$  and sublimed in vacuo without alteration at  $230-45^{\circ}$ . This ester is also dextro-rotatory, the value in chloroform being  $(\alpha)_{546.1}^{26} 57.1^{\circ} (c=1.654)$ .

Friedelin  $\beta$ -phenylpropionate crystallized from acetone-benzene mixture in small short needles which melted after sublimation in vacuo at  $229-33^{\circ}$ . The temperature in the furnace during sublimation was  $230-5^{\circ}$ . The ester is dextro-rotatory, the value in chloroform being somewhat lower than the others,  $(\alpha)_{546.1}^{23} 52.8^{\circ} (c=1.022)$ . It is interesting to note that as the phenyl group is each time removed one  $\text{CH}_2$ - further from the friedelin molecule, the rotation decreases markedly.

Friedelin p-iodobenzoate crystallized in the form of small needles from alcohol-benzene mixture to melt at  $271-4^{\circ}$ . The rotation in chloroform was  $(\alpha)_{546.1}^{25} 61.2^{\circ} (c=1.258)$ . No attempt was made to sublime the substance in vacuo.

Friedelin phenylacetate may be saponified easily and cleanly with sodium n-propylate in n-propyl alcohol to yield

a crystalline product. Friedelin thus purified by conversion to an ester and subsequent saponification crystallized from ethyl acetate, alone or with benzene, in brilliant flat needles melting at  $255-61^{\circ}$  with very gradual decomposition, the melting point remaining the same after sublimation in vacuo at  $225-30^{\circ}$ . Elementary analysis of friedelin indicated the formula  $C_{30}H_{50}O$ .

The optical data in the case of friedelin is as follows:

Habit: Broad laths.  
Extinction: Parallel elongation.  
 $B_x$ : Character positive; angle moderately large and perpendicular to the broad face of the lath.  
Indices of refraction:  $\alpha = 1.550$ ,  $\beta = 1.575$ ,  $\gamma = 1.620^a$   
( $B_x$  figure centered)  
Density: 1.078.

From the root mean square index of refraction and the density, the value  $M_R = 132.0$ , while that calculated<sup>51</sup>, assuming one double bond and ketonic oxygen was 131.9. The presence of a double bond in the friedelin molecule was further demonstrated by the yellow color produced when a chloroform solution of the material was treated with tetra-nitro methane.

Pure friedelin when subjected to the action of the

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<sup>a</sup> White light.

Grignard reagent in the Zerwitenoff determination<sup>a</sup> showed no active hydrogen. The material is not then an alcohol as was at first supposed, but probably a ketone. This conjecture has recently been shown to be the true case as a result of the work of Shrader<sup>48</sup> who has succeeded in preparing several carbonyl derivatives of friedelin, and by Campbell who has reduced friedelin to the corresponding carbinol.

Since friedelin is a ketone it is necessary for esterification to take place through an enol form. This fact seems in accord with a consideration of the rather drastic treatment to which the friedelin must be subjected in order for ester formation to occur. A sample of friedelin obtained directly from the crude extracted material by a tedious series of recrystallizations and one which had been purified through the phenylacetate were identical in every respect with a sample of the latter which had further been converted to the benzoate and saponified. No unexpected alteration is therefore undergone by the friedelin molecule during these transformations and saponification of the friedelin esters regenerates the ketone.

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<sup>a</sup>The author is indebted to Dr. A. H. Blatt of Howard University for this determination.

Friedelin is much less optically active than cerin, the rotation in chloroform like that of cerin is about one half the value reported by Istrati and Ostrogovich being  $(\alpha)_{5461}^{23} -29.4^{\circ} (c=3.046)$ ,  $(\alpha)_{5461}^{20} -29.4^{\circ} (c=7.257)$ . Moreover, as can be seen, the rotation of friedelin as well as that of cerin does not appear to change with concentration as reported by these workers.

Friedelin reacts readily with bromine with the evolution of HBr. Several bromo derivatives are apparently formed concurrently since the products are complex mixtures containing varying amounts of bromine depending upon the bromination solvent and temperature and the quantity of bromine used. No pure mono-, di- or tribromo- derivative could be isolated although in every case the product was crystalline.

The molecular weight of friedelin was determined from the saponification of certain esters and from the analysis of the p-iodobenzoate.

The method employed for the quantitative saponification of the friedelin esters was essentially that of Char-gaff<sup>49</sup>. Operating in this manner the molecular weight could easily be determined with enough precision to definitely settle the question of the number of carbon atoms in the friedelin molecule. The following table presents a

summary of the data from the saponification studies, calculated back to give the rounded off values for the molecular weight of friedelin.

Table IV. Summary of the data obtained in the saponification of the friedelin esters.

Ester	Mol. Wt. Friedelin.
Friedelin acetate - - - -	422, 430, 423.
" benzoate - - - -	419, 430, 426, 422.
" phenylacetate - -	420, 429, 430, 429, 427.
" $\beta$ -phenylpropionate -	427, 424.
	Mean value - - 425.
	Calcd. for $C_{30}H_{50}O$ - 426.

The difference in the iodine content of the p-iodobenzoates of friedelin of the two possible formulas,  $C_{29}H_{48}O$  and  $C_{30}H_{50}O$ , is 0.44%. Analysis of friedelin p-iodobenzoate gave values varying only 0.16% and 0.01% from that calculated for  $C_{30}H_{49}OCOC_6H_4I$ .

Carbon and hydrogen values are more helpful in distinguishing between the possible formulas,  $C_{30}H_{48}O$ ,  $C_{30}H_{50}O$  and  $C_{30}H_{52}O$  than in deciding between  $C_{29}H_{48}O$  and  $C_{30}H_{50}O$  where the difference is one  $CH_2$ - group. The observed analytical values for friedelin coincide closely with those calculated for  $C_{30}H_{50}O$  but do not definitely exclude the other two possible formulas, each of which differs from the

above by but two hydrogen atoms.

Neither friedelin nor cerin display the true sterol colors, though cerin does give a faint red color in the Liebermann-Burchard reaction. The fact that the early workers obtained a positive test for sterol with cerin was undoubtedly due to the presence of some impurity of sterol nature.

In the treatment of 220 grams of the crude extracted solid with alcoholic potassium hydroxide, it was noted that the concentration of the alcoholic alkaline filtrate deposited some gelatinous material which gave strong colors in the Liebermann test. The material was very soluble in alcohol and, after repeated attempts to crystallize it from this solvent, was obtained in the form of a colorless gel which dried, in vacuo over phosphorous pentoxide, to a pasty amorphous white solid. Sublimation in vacuo at 130-40° yielded an amorphous white solid melting at 65-70° to a turbid liquid which became clear at 145°. The substance appeared on the basis of carbon and hydrogen analyses to have the formula  $C_{28}H_{50}O_2$ . The total weight of material isolated was 25 milligrams. It absorbed bromine in carbon tetrachloride solution and gave the following results when subjected to the sterol color tests:

Liebermann-Burchard<sup>52</sup>; Rose red color changing to purple, then deep blue and finally bright emerald green.

Salkowski<sup>53</sup>; Yellow which changed to a deep orange red.

Lifschütz<sup>54</sup>; Faint pink changing slowly to a light purplish brown.

## EXPERIMENTAL

### Isolation of Cerin.

50 pounds of 20-30 mesh ground cork extracted with ethyl acetate as already described, yielded about 1.5% its weight of dry nearly white crude cerin and friedelin mixture. Two recrystallizations of this material from chloroform sufficed to separate most of the friedelin. The less soluble cerin, after one recrystallization from benzene followed by two further recrystallizations from chloroform was obtained in the form of fine silky needles which melted at  $247-51^{\circ}$ . A sample of this material was sublimed in vacuo at  $210-30^{\circ}$  for analysis.

Anal. Subs., 3.130, 3.112, 2.534 mg.:  $\text{CO}_2$ , 9.357, 9.310, 7.561 mg.;  $\text{H}_2\text{O}$ , 3.268, 3.201, 2.619 mg.

Calcd. for  $\text{C}_{30}\text{H}_{48}\text{O}_2$ : C, 81.74; H, 10.99.

Calcd. for  $\text{C}_{30}\text{H}_{50}\text{O}_2$ : C, 81.38; H, 11.39.

Calcd. for  $\text{C}_{30}\text{H}_{52}\text{O}_2$ : C, 81.01; H, 11.75.

Found: C, 81.53, 81.58, 81.38; H, 11.68, 11.51, 11.56.

### Isolation of "friedelin rich" material.

By concentrating the chloroform filtrates, from the first two recrystallizations of the crude, until solid material separated and then adding an equal volume of acetone, the crude friedelin was precipitated as a crystalline powder. This solid, containing some colored matter,

yielded pure friedelin upon conversion to the benzoate or phenylacetate and saponifying.

Friedelin benzoate-.

10.0 g. of "friedelin rich" material was heated with 20.0 ml. of benzoyl chloride on an oil bath from 150-85° during an interval of 45 min. To the somewhat cooled reaction mixture was cautiously added 150 ml. of 95% alcohol. The solid material was broken up and digested on the steam bath for 10-15 min. after which the warm suspension was filtered and the solid re-treated with 100 ml. alcohol. Recrystallization from ethyl acetate-benzene yielded 7.0 g. of brilliant flat needles or leaves, a sample of which after sublimation in vacuo at 240-5° melted at 255-62°. Anal. Subs., 4.032, 3.895, 3.761 mg.: CO<sub>2</sub>, 12.366, 11.943, 11.523 mg.; H<sub>2</sub>O, 3.724, 3.596, 3.453 mg. Calcd. for C<sub>30</sub>H<sub>48</sub>OCOC<sub>6</sub>H<sub>5</sub>: C, 83.71; H, 10.26. Found: C, 83.64, 83.62, 83.56; H, 10.33, 10.33, 10.27.

Saponification of friedelin benzoate with alcoholic NaOH in C<sub>5</sub>H<sub>5</sub>N.

2.0 g. of friedelin benzoate was refluxed in 25 ml. of pyridine containing 60 ml. of 0.1N alcoholic NaOH. The solution was homogeneous after 19 min. whereupon the liberated friedelin began to separate from the solution.

After heating for one hour the solution was cooled, the yellow crystalline material filtered off, redissolved in  $\text{CHCl}_3$  and washed with dilute  $\text{H}_2\text{SO}_4$  and water. The chloroform layer was then dried and evaporated and the solid residue recrystallized from ethyl acetate to yield 1.3 g. of white needles. A sample on sublimation in vacuo at  $225-30^\circ$  melted at  $255-61^\circ$ .

Anal. Subs., 3.423, 4.057, 4.943 mg.:  $\text{CO}_2$ , 10.584, 12.579, 15.332 mg.;  $\text{H}_2\text{O}$ , 3.612, 4.303, 5.248 mg.

Calcd. for  $\text{C}_{30}\text{H}_{48}\text{O}$ : C, 84.82; H, 11.40.

Calcd. for  $\text{C}_{30}\text{H}_{50}\text{O}$ : C, 84.43; H, 11.82.

Calcd. for  $\text{C}_{30}\text{H}_{52}\text{O}$ : C, 84.03; H, 12.23.

Found: C, 84.33, 84.57, 84.59; H, 11.81, 11.87, 11.88.

Friedelin phenylacetate.

25.0 g. of "friedelin rich" material was heated with 40.0 ml. of phenylacetyl chloride on an oil bath from  $150-85^\circ$  during an interval of 45 min. To the warm melt was cautiously added 200 ml. of 95% alcohol. The solid was broken up and digested for 10-15 min. on the steam bath, filtered off and re-treated with 200 ml. alcohol. Recrystallization from benzene-ethyl acetate yielded 19.0 g. of stubby white needles, a sample of which after sublimation in vacuo at  $230-40^\circ$  melted at  $244-51^\circ$ .

Anal. Subs., 3.220, 4.535 mg.: CO<sub>2</sub>, 9.897, 13.950 mg.;  
H<sub>2</sub>O, 3.031, 4.241 mg.

Calcd. for C<sub>30</sub>H<sub>40</sub>OCOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>: C, 83.77; H, 10.36.

Found: C, 83.81, 83.89; H, 10.53, 10.46.

Saponification of friedelin phenylacetate with sodium n-propylate in n-propyl alcohol.

10.0 g. of friedelin phenylacetate was refluxed for one hour in 500 ml. of n-propyl alcohol containing 0.6 g. of sodium. The mixture was homogeneous after 10 min. boiling whereupon crystalline material began to separate. The reaction mixture was cooled and filtered to give 6.5 g. of nearly white needles. An additional 0.5 g. was obtained by concentrating the filtrate. Recrystallization from ethyl acetate yielded perfectly white flat needles melting at 255-61°.

Friedelin  $\beta$ -phenylpropionate.

2.0 g. "friedelin rich" material was heated with 5.0 ml. of  $\beta$ -phenylpropionyl chloride on an oil bath from 150-85° During a 45 min. interval. The reaction mixture was cooled somewhat, treated with ethyl alcohol to destroy the excess acid chloride and the solid product recrystallized from ethyl acetate. Sublimation of the solid material in vacuo at 240-5° followed by further recrystallization from ac-

etone-benzene mixture yielded fine white needles melting at 229-33°.

Anal. Subs., 3.861, 4.625 mg.: CO<sub>2</sub>, 11.866, 14.222 mg.; H<sub>2</sub>O, 3.674, 4.339 mg.

Calcd. for C<sub>30</sub>H<sub>49</sub>OCOCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>: C, 83.63; H, 10.46.

Found: C, 83.81, 83.87; H, 10.65, 10.50.

Friedelin p-iodobenzoate.

1.0 g. of friedelin was mixed with 3.0 g. of molten p-iodobenzoyl chloride, after which the mixture was heated on an oil bath from 150-75° during an interval of 30 min. The resulting solid was worked up in a manner similar to that for the other esters. Recrystallization from benzene-alcohol yielded 0.7 g. of flat white needles, which after further recrystallization from benzene-ethyl acetate melted at 271-4°.

Anal.<sup>a</sup> Subs., 3.915, 2.889 mg.: CO<sub>2</sub>, 9.750, 7.190 mg.; H<sub>2</sub>O, 2.901, 2.067 mg.

Calcd. for C<sub>30</sub>H<sub>49</sub>OCOC<sub>6</sub>H<sub>4</sub>I: C, 67.65; H, 8.14.

Found: C, 67.92, 67.87; H, 8.29, 8.01.

Anal. Subs., 11.508, 12.917 mg.: AgI, 4.115, 4.583 mg.

Calcd. for C<sub>30</sub>H<sub>49</sub>OCOC<sub>6</sub>H<sub>4</sub>I: I, 19.34. Calcd. for C<sub>29</sub>H<sub>47</sub>O-COC<sub>6</sub>H<sub>4</sub>I: I, 19.76.

Found: I, 19.33, 19.18.

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<sup>a</sup>The writer wishes to thank S.A. Shrader for these Carbon-hydrogen analyses.

Saponification equivalents of the friedelin esters.

The method used for the determination of the saponification equivalents was that of Chargaff<sup>49</sup> with slight modification as follows: 40-80 mg. of the ester was saponified by refluxing for 30 min. with 10 ml. of 0.05N sodium n-propylate in n-propyl alcohol. The ground glass tip of the condenser was washed down with 10 ml. of water; the aqueous alcohol containing suspended friedelin was then cooled and titrated.

Table V. gives a summary of the saponification data obtained.

HCl treatment of cerin-.

3.0 g. of cerin was suspended in 70 ml. of chloroform and dry HCl passed into the suspension at 15-20°. All the cerin had dissolved after 10-15 min. treatment. HCl was passed in for one hour after which the reaction flask was closed with a CaCl<sub>2</sub> tube and allowed to stand over night at room temperature. The chloroform was then removed by aspirating dry air through the solution and the sticky white residue washed out of the reaction flask with 50 ml. of dry ether. This solution was filtered and diluted with an equal volume of absolute alcohol. By alternately evaporating the solution and cooling it in a Dewar flask with

Table V. Saponification data obtained for the friedelin esters.

Ester	Subs. (mg.)	Blank ml. Acid	Acid + to Alk. used.	CologN Mol. Wt. Ester	Mol. Wt. Friedelin
Benzoate	71.152	4.75	2.33	0.2337	523.0
	55.798	"	1.79	"	533.8
	46.301	6.08	1.49	.2319	530.0
	67.248	"	2.18	"	526.1
Phenyl- acetate	73.760	8.14	2.35	.2337	537.5
	73.185	"	2.29	"	547.4
	66.930	"	2.09	"	548.4
	58.882 <sup>a</sup>	---	2.07	.28358	546.9
	39.686	---	1.40	"	544.6
-Phen- ylpropion- ate	77.688	8.14	2.33	.2337	559.1
	82.494	"	2.54	"	556.3
Acetate <sup>b</sup>	56.023	6.07	2.06	.2319	463.9
	86.825	6.12	3.14	"	471.6
	68.628	"	2.52	"	464.5

solid CO<sub>2</sub>, the following crops of white amorphous solid were obtained:

1	-	-	-	-	-	0.5 g.	m.p. 227-34 <sup>o</sup> (uncor.)
2	-	-	-	-	-	0.9	187-93 <sup>o</sup>
3	-	-	-	-	-	0.9	180-6 <sup>o</sup>
4	-	-	-	-	-	0.2	186-99 <sup>o</sup>
5	-	-	-	-	-	0.2	184-95 <sup>o</sup>

The combined solid material from crops 2, 3, 4, and 5, aggregating 2.2 g. was recrystallized from 1:1 ether-absolute alcohol to give an amorphous white solid(I)

<sup>a</sup>The author wishes to thank S.A. Shrader for the last two determinations made on the phenylacetate.

<sup>b</sup>A sample of ester prepared by S.A. Shrader.

melting at 196-201° with the rapid evolution of HCl. When a portion of I was sublimed in vacuo at a temperature of 190-200°, the sublimate consisted of a brittle, non-crystalline film(II) which melted partially at 100-110°, re-solidified below 150° and remelted to a clear liquid at 195-200° with the rapid evolution of HCl. A small amount of halogen free residue melting at 240°(uncor.) was left in the sublimation chamber. When a sample of II was heated to 150° and then mixed with I, the mixture was observed to melt clear, with the evolution of HCl, at 193-200°.

Anal. Subs., (I) 3.344, 4.435 mg.: CO<sub>2</sub>, 9.693, 12.859; H<sub>2</sub>O, 3.295, 4.304. mg. Calcd. for C<sub>30</sub>H<sub>49</sub>OCl: C, 78.11; H, 10.72. Found: C, 79.05, 79.07; H, 11.03, 10.86.

Subs., (II) 2.797 mg.: CO<sub>2</sub>, 8.231 mg.; H<sub>2</sub>O, 2.845 mg. Found: C, 80.26; H, 11.38.

Subs., (I) 8.476 mg.: AgCl, 2.497 mg. Calcd. for C<sub>30</sub>H<sub>49</sub>OCl: Cl, 7.70. Found: Cl, 7.29.

#### Bromination of friedelin.

In the typical bromination experiment, 0.5 to 2.0 g. of friedelin was suspended or dissolved in 200 ml. of the solvent and a calculated amount of bromine in CHCl<sub>3</sub>, CCl<sub>4</sub> or HOAc added. The reaction mixture was stirred for one hour after the addition and the solid material obtained

was recrystallized from dry benzene mixed with ethyl acetate, acetone, or absolute alcohol. The products obtained were crystalline but possessed varying melting points and composition, depending upon the solvent, temperature and quantity of bromine used, as shown in Table VI.

Table VI. A summary of the studies of the bromination of friedelin.

Solvent	Quant. Br.	Temperature	M.p. Product	%Br
10%HOAc in ether	2 mols	0-20°	176-7°	15.53, 15.35
"	"	20-30°	182-5°	20.47, 20.66
Chloroform	Equimol.	10-15°	215-6°	10.55, 10.69
"	4 mols	20°	210.5°	24.40
HOAc	Equimol.	45-55°	201-3°	16.43, 16.28 <sup>a</sup>
CCl <sub>4</sub>	4 mols	50°	198-9°	30.64
Anal.	Subs. mg.	AgBr mg.	%Br	
	4.160	1.518	15.53	
	5.388	1.943	15.35	
	6.753	3.249	20.47	
	7.201	3.496	20.66	
	4.809	1.193	10.55	
	9.165	2.303	10.69	
	9.730	5.580	24.40	
	9.151	3.535	16.44	
	9.164	3.505	16.27	
	8.850	6.374	30.65	

Calcd. for C<sub>30</sub>H<sub>49</sub>OBr: Br, 15.81. Calcd. for C<sub>30</sub>H<sub>48</sub>OBr<sub>2</sub>: Br, 27.34. Calcd. for C<sub>30</sub>H<sub>47</sub>OBr<sub>3</sub>: Br, 36.21.

<sup>a</sup>The author takes this opportunity to thank W. P. Campbell for these bromine analyses.

Isolation of the sterol.

Upon the recovery of the alcohol from the alkaline filtrates left after the alcoholic potassium hydroxide treatment of 220 g. of the crude extracted material, there remained a gelatinous residue. The material was very soluble in alcohol and could be precipitated from cold alcohol as a gelatinous solid. The bulk of the brown colored matter was removed from this material by repeated attempts to recrystallize it from absolute alcohol. The white gel thus obtained was dried in vacuo and sublimed in vacuo at 130-40° to yield about 25 milligrams of a fluffy amorphous solid, which melted at 65-70° to a turbid liquid which cleared at 145°. The same melting point was observed on remelting.

Anal. Subs., 2.860, 2.428 mg.: CO<sub>2</sub>, 8.441, 7.164 mg.:  
H<sub>2</sub>O, 3.081, 2.630 mg.

Calcd. for C<sub>27</sub>H<sub>48</sub>O<sub>2</sub>: C, 80.12; H, 11.97.  
Calcd. for C<sub>28</sub>H<sub>50</sub>O<sub>2</sub>: C, 80.30; H, 12.05.

Found: C, 80.48, 80.46; H, 12.05, 12.12.

### SUMMARY

1. The extraction of cork with ethyl acetate yields a crystalline material consisting of a mixture of friedelin and cerin, separable, as observed by Istrati and Ostrogovich, by virtue of the difference in solubility of the two compounds in chloroform.
2. Cerin purified by recrystallization from chloroform and benzene and sublimation in vacuo, appears, on the basis of carbon and hydrogen analyses to have the formula  $C_{30}H_{50}O_2$  first proposed by Thoms.
3. Friedelin, a ketone, most easily purified through the enolbenzoate or enolphenylacetate, is considered, on the basis of analytical data and the saponification of certain of its esters, to have the formula  $C_{30}H_{50}O$ .
4. Friedelin reacts with bromine with the evolution of HBr to yield a mixture of bromination products, the halogen content of which varied with the bromination, solvent, temperature and the quantity of bromine used. No pure mono-, di-, or tribromo- derivative could be isolated.
5. Cerin appears to contain a tertiary hydroxyl group. It reacts with dry HCl to give a soluble halogen containing derivative. It proved impossible to isolate a perfectly pure monochloro derivative due probably to the lability

of the chlorine atom in the cerin molecule.

6. A third compound, of sterol nature, has been found as a constituent of the crude extracted material from cork.

The substance appears, on the basis of carbon and hydrogen analyses to have the formula  $C_{28}H_{50}O_2$ .

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