hours, saponification took place. The solvent was evaporated, the potassium salt acidified and β-(3-pyrenyl)-crotonic acid recrystallized from ethyl malonate; m. p. 233°. *Anal.* Found: C, 83.5; H, 5.2. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9.

Pyrene and β-Chlorobutyryl Chloride.—At room temperature and under constant stirring, β-chlorobutyryl chloride (14 g.) was added slowly to a mixture of pyrene (20 g.), carbon disulfide (75 cc.) and aluminum chloride (30 g.). The mass was stirred for two more hours, and decomposed with ice and concentrated hydrochloric acid. The carbon disulfide solution was washed with sodium carbonate solution, dried and distilled. The *ketone* (VI?) formed distilled at 170° under 0.02 mm. pressure, and after trituration with methyl alcohol was recrystallized from the same solvent and from low-boiling light petroleum; m. p. 101°. *Anal.* Found: C, 88.4; H, 5.4. Calcd. for $C_{20}H_{14}O$: C, 88.9; H, 5.2.

Summary

Pyrene adds two atoms of lithium, C_4 and C_9 or C_3 and C_{10} being the most likely positions. Carbonation gave a dihydro-pyrene-dicarboxylic acid.

Some reactions of β-(3-pyrenyl)-acrylic acid have been studied. With diazomethane, besides esterification, methylation occurs at the β-carbon atom.

With β-chlorobutyryl chloride and aluminum chloride, pyrene gives a keto-cyclopenteno derivative, probably of formula (VI). The analogous reaction of anthracene leads to two isomeric ketones $C_{18}H_{14}O$.
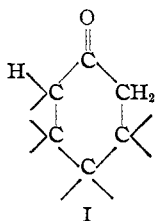

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Cerin and Friedelin. VI. Surface Films of Cerin, Friedelin and Some Related Substances

BY NATHAN L. DRAKE AND JOHN K. WOLFE[1]

Previous work[2] has shown that friedelin is a polycyclic triterpenoid ketone, $C_{30}H_{50}O$, containing the unit of structure, I.

I

Dehydrogenation of friedelinol, the carbinol corresponding to friedelin, has not yielded isolable oxygen-containing fragments from which the location of I in the polymethylperhydropicene nucleus might be inferred. It is the purpose of the present paper to describe studies of surface films of certain relatives of friedelin. From these investigations we have been able to draw certain general conclusions regarding the position of the carbonyl group in friedelin.

Dehydrogenation of friedelinol yields: 1,2,7-trimethylnaphthalene, 1,2,5-trimethylnaphthalene, 1,2,5,6-tetramethylnaphthalene (in small quantity), 1,2,8-trimethylphenanthrene and 1,8-

dimethylpicene.[3] The carbon skeleton, II, proposed by Ruzicka for oleanolic acid[4] explains the formation of these dehydrogenation products fairly satisfactorily.

II
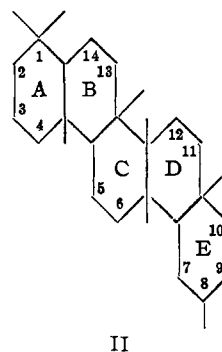
The unit, I, might be located in II with its carbonyl at one of the three positions 14, 5, or 9. Position 14, 5, or 9 (cpd. III) is most satisfactory in the light of the surface film studies described below, but the carbonyl of friedelin cannot be here because friedonic acid, the keto acid obtained from friedelin by oxidation, has a hydrogen atom on the carbon adjacent to its carbonyl group.[2b] Position 5 (cpd. IV) is an unsatisfactory location for the

(1) From the Ph.D. dissertation of John K. Wolfe. University of Maryland. 1939.

(2) Drake and Campbell. (a) THIS JOURNAL. **58**, 1681 (1936); (b) Drake and Wolfe, *ibid.*, **61**, 3074 (1939).

(3) Drake and Haskins, *ibid.*, **58**, 1684 (1936); Houston, Dissertation, University of Maryland, 1938.

(4) Ruzicka. Goldberg and Hofmann. *Helv. Chim. Acta*, **20**, 325 (1937).

carbonyl group of friedelin for the same reason and also because of the results of our surface film studies. Position 9 (cpd. V) is unsatisfactory from the standpoint of our surface film studies, because of the extreme unreactivity of the carbonyl group of friedonic acid, and because friedonic acid does not respond to the haloform test. It seems necessary, therefore, to seek some other carbon skeleton than II to represent friedelin. Such a formula will be discussed below.

Friedelin itself was found unsatisfactory for surface film pressure measurements because of the extreme instability of the film (curve I, Fig. 1). Films of friedelinol, the corresponding alcohol, and of friedelin oxime, however, yielded satisfactory films which occupied areas of about 53.0 and 53.5 sq. Å., respectively, at zero compression. Figure 1 shows the relation between area per molecule and pressure applied to films of friedelin, friedelinol, friedelin oxime and friedonic acid. The area occupied per molecule by a film of friedonic acid at zero compression is larger by about 3 sq. Å. than that occupied by either friedelinol or friedelin oxime.
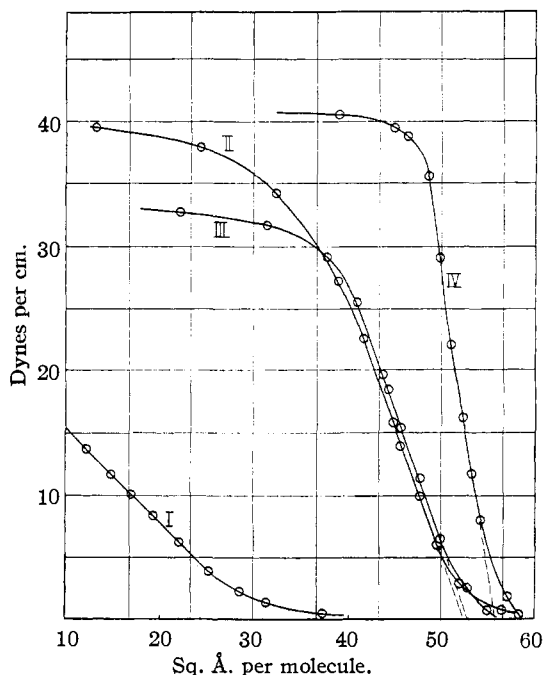

Fig. 1.—Pressure–area curves for surface films of: I, friedelin; II, friedelinol; III, friedelin oxime; IV, friedonic acid.

When friedonic acid is spread upon 0.02 N sodium hydroxide, the molecules lie nearly flat on the surface due to the strong attraction of the

alkali for the carboxyl group (Fig. 2). Films of norfriedonic acid[2b] behave in the same way. However, films of friedelin oxime occupy approximately the same area per mole at zero compression whether they are spread upon distilled water or upon dilute alkali. If the oximino group were in ring C, the small area per mole of friedelin oxime at zero compression might be explained by the assumption that the molecules were on the surface at an angle due to the weak anchorage from ring C. If this were the case, then the area per molecule of films spread on alkali should be much larger due to the enhanced attraction of the surface for the oximino group. Since this is not the case, it is concluded that the oximino group must be near the end of the molecule.
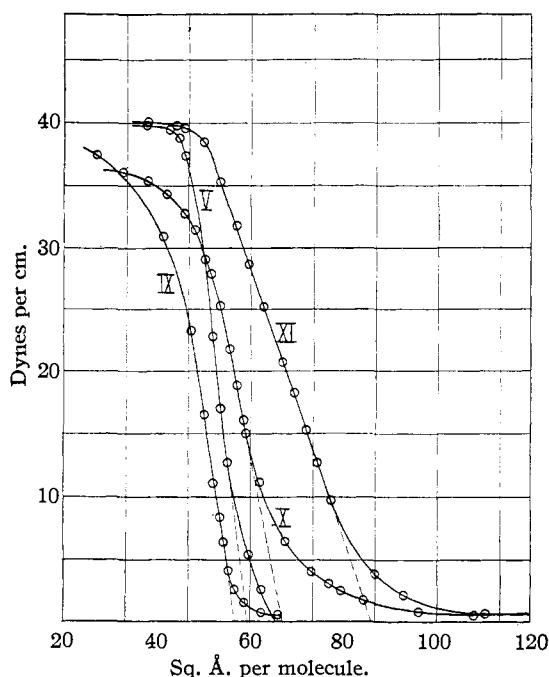

Fig. 2.—Pressure–area curves for surface films of: V, norfriedonic acid; IX, friedelin oxime; X, norfriedonic acid; XI, friedonic acid. Curves IX, X and XI refer to films on 0.02 N sodium hydroxide; curve V to a film on distilled water.

Scale models indicate that III should cover a surface area of 56–60 sq. Å. per molecule, that IV should lie flat and occupy an area of 110–120 sq. Å. per molecule, and that V should stand on end and occupy an area of about 47–48 sq. Å. per molecule.

Askew[5] has studied surface films of β-amyrin. This substance forms stable films in which the

(5) Askew, J. Chem. Soc., 1585 (1936).

area covered per molecule is 47 sq. Å. Even β-amyrone, with its weakly hydrophilic carbonyl group, gives a very slightly compressible film which occupies an area of 49.5 sq. Å. per molecule. The hydroxyl group of amyrin occupies the 2-position in the perhydropicene nucleus.[6] One would predict that surface films of the carbinol from V should correspond fairly closely in area per mole to those of a similar substance whose hydroxyl group is at C_2 (*i. e.*, amyrin). Our investigations show that the area per mole of friedelinol in surface films is considerably greater than that of amyrin as determined by Askew, and it seems, therefore, that V is an unsatisfactory formula for friedelin.

Were it not for the fact that friedonic acid is capable of enolization, III might well represent friedelin. If it is assumed that the molecules lie on the surface at a slight angle, measured and calculated areas would agree very closely. If this picture is correct, friedonic acid, in which a ring has been ruptured producing a strongly hydrophilic group farther from the end of the molecule, should occupy a larger area per mole in a surface film than friedelinol. The results of our experiments are in accord with this prediction.
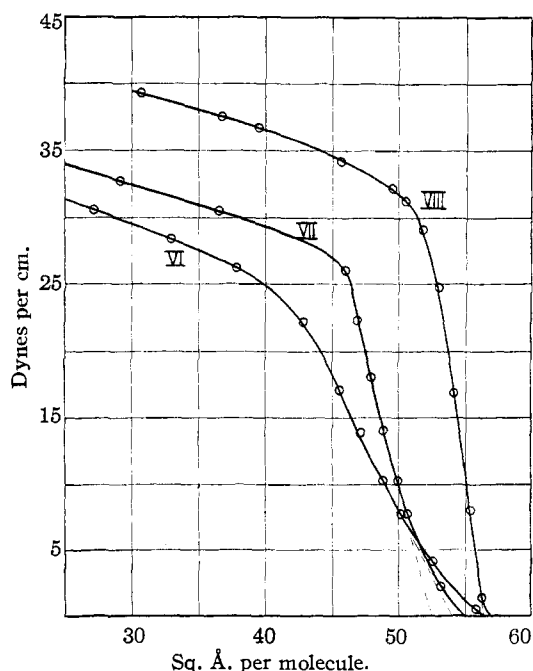

Fig. 3.—Pressure–area curves for surface films of: VI, cerin; VII, dihydrocerin; VIII, a dibasic acid obtained from cerin by oxidation.

Of the various structures which have been suggested as possible triterpenoid nuclei, that of Z. Kitasato,[7] VI, with a >CHOH group in either of the positions starred, permits a reasonable interpretation of our surface film data. This structure is not so satisfactory, however, in explaining the products of dehydrogenation of friedelinol.
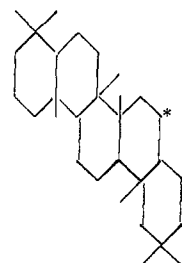
VI

It does not seem worth while, at the present stage of our knowledge concerning friedelin, to discuss the various other structures which have been suggested as possible triterpenoid nuclei; for our purpose all are deficient in one respect or another. We should like to point out, however, that our experimental evidence indicates quite clearly that the functional group of friedelin is certainly not in ring C, and that our surface film studies could be explained if the carbonyl were at C_{11} or C_{14} of a polymethylperhydropicene nucleus whose methyl groups were so located as to permit enolization of friedonic acid.

Figure 3 shows the relation between area per molecule and applied pressure for films of cerin (curve VI), dihydrocerin[8] (curve VII), and a dibasic acid[9] formed from cerin by oxidation without loss of carbon. The areas covered by these substances in films at zero compression are 54, 52.5 and 56.5 sq. Å. in the order given above.

It is at once apparent from a comparison of these values with those obtained from films of friedelin derivatives that the hydroxyl group of cerin is not far removed from the carbonyl[10]; indeed, there is a considerable amount of chemical evidence,[9] which will be presented in a later paper, that these two groups are adjacent.

Experimental

The surface film pressures were first measured on a balance of the type described by Adam and Jessup,[11] and later

(6) Ruzicka and Hofmann, *Helv. Chim. Acta.* **20**, 1155 (1937).

(7) Z. Kitasato. *Acta Phytochim.* (Japan), **10**, 199 (1937).

(8) Drake and Shrader. THIS JOURNAL. **57**, 1854 (1935).

(9) G. K. Holmes. unpublished results.

(10) It has been shown[8] that the carbonyl group occupies the same position in both cerin and friedelin.

(11) Adam and Jessup, *Proc. Roy. Soc.* (London), **110**. 423 (1926).

on a Cenco Hydrophil balance. Data obtained on one instrument were in good agreement with those obtained on the other.

The general procedure was that developed by Adam, Askew and Danielli.[12] A 1–2 mg. sample, weighed to 0.005 mg., was dissolved, at room temperature, in carefully purified benzene, and the volume of the solution was adjusted to 25 ml. in a volumetric flask. The solution was placed on the surface by means of a calibrated 1-ml. pipet. The films described by curves I through VIII were spread on distilled water; curves IX. X, and XI concern films which were spread on 0.02 N sodium hydroxide. Each film was studied at room temperature (21–26°).

All of the films studied showed the phenomenon of contraction, and contraction was most pronounced in films of friedelinol and cerin. Films of the acidic substances were very stable but showed some contraction at high pressures. The films reported are equilibrium films.

To check our technique and procedure, data were obtained for films of carefully purified stearic acid. These data agreed very well with those of Adam and co-workers.[13]

Summary

1.   Measurements of pressure–area relations of surface films of friedelin and some of its derivatives indicate that the functional group is located near the end of the molecule, certainly not in ring C.

2.   A study of surface films of cerin and certain of its derivatives indicates that the hydroxyl and carbonyl groups are not far removed from each other in the molecule.

(13) N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, New York, N. Y., 1938, page 50.

COLLEGE PARK, MARYLAND   RECEIVED APRIL 3, 1940

(12) Adam, Askew and Danielli, *Biochem. J.*, **29**, 1786 (1935).

The Photolysis of Ethyl Iodide in Various Solvents

BY W. WEST AND J. FITELSON[1]

The photo-decomposition of the lower alkyl iodides is one of the few photo-reactions at present known in which the quantum yield is greater in the liquid state[2a] or in solution[2b] than in the dilute gaseous state. Ethyl iodide, for instance, undergoes photolysis at wave length 2537 Å., with a yield in the liquid state or in hexane solution, of about 0.4 atom of iodine produced per photon absorbed, while in the gaseous state the yield is less than 0.01. The present study is an attempt to secure further experimental information which might aid in understanding the effect of the medium on photo-reactions by observing the photolysis of ethyl iodide in a series of solvents of varied physical and chemical characteristics, namely, hexane, carbon tetrachloride, chloroform, benzene, chlorobenzene, carbon disulfide, ethyl alcohol, diethyl ether, acetic acid, ethyl acetate, methyl iodide and certain mixtures. Most of the experiments were performed at wave lengths embracing the region from about 2800 to 2537 Å., with an energy center at 2610 Å.; hexane solutions were also studied at wave length 2026 Å., and some observations were made at wave length 3130 Å.

Experimental Details.—The apparatus consisted of the normal photochemical set-up of source, quartz lenses, light filters, quartz reaction cell and thermopile–galvanometer system.

Light Sources.—For wave length 2610 Å., a 220-volt mercury arc was used whose light was filtered by 3 cm. of chlorine at one atm., 5 cm. of bromine vapor at a little under its saturation pressure at room temperature and 5 cm. of normal acetic acid, all in separate vessels. The range transmitted was from 2800 to 2537 Å., with an energy center at 2610 Å. For wave length 2026 Å., light from a zinc spark was monochromatized by focal isolation. The absorption of ethyl iodide was such that only the line at 2026 Å. was chemically effective. For wave length 3130 Å., glass vessels were exposed to the full light of the mercury arc. The transmission of the glass and the absorption of the iodide solutions were such as to make most of the actinic action originate in the line at 3130 Å.

Energy measurements were made by the integration method[3] by means of a Moll linear thermopile and Zernicke Zc galvanometer. Calibration was frequently made against Bureau of Standards carbon filament standards. No change in calibration with time occurred.

Determination of Iodine Produced.—This was effected photometrically by means of a Weston Photronic cell, a Leeds and Northrup type P galvanometer of 1000 ω resistance, a 21 candle power automobile lamp lit by a storage battery floated on the line, and the necessary filters, lens and stops arranged so as to permit analysis *in situ* during a run. The filters for violet or red iodine solutions consisted of 8-mm. thicknesses each of saturated

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(2)   (a) B. M. Norton, THIS JOURNAL, **56**, 2294 (1934); (b) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(3)   P. A. Leighton and W. G. Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).