The Rearrangement of Molecules in Plastic Monomolecular Films: Pressure–Area and Potential Relations for Polycyclic Compounds of the Five-Ring Series

BY WILLIAM D. HARKINS, EVERETT F. CARMAN AND HERMAN E. RIES

1. Introduction

Monomolecular films of certain compounds whose molecules contain five benzene rings have been found to exhibit a remarkable phenomenon. That is, a rapid rearrangement of the molecules occurs in the film in such a way that the pressure at the initial area almost disappears. Thus with betuline the initial or immediate pressure at a molecular area of 34.5 sq. Å. is 17 dynes per cm. while after this there is at this area an almost exponential fall of pressure with time to a practically constant value of 1.0 dyne. Nevertheless, a rapid compression to 33.5 sq. Å., or by about $1/_{34}$ of the area, increases the pressure by 21 times to 21 dynes, or to 4 dynes more than the previous initial compression. At an area of 28 sq. Å. the initial pressure of 40 dynes falls to 5.5 dynes in thirty seconds, but on rapid compression to 26.2 sq. Å. rises to 50 dynes per cm.

The set of six polycyclic compounds was made available through the kindness of Professor Ruzicka. The molecules of these compounds contain a phenanthrene residue (Figs. 1 and 2) as did the *d*-pimaric acids (Fig. 3) investigated in this Laboratory by Harkins, Ries and Carman.[1] A comparison of the surface potentials and force-area relations of the monomolecular films formed by this series (Figs. 4, 5, 6) is of considerable value, since the compounds (supposedly) differ only in their polar substituents.

The writers had the privilege of discussing the proposed structures with Professor Ruzicka (August, 1935), who tentatively assigned the polar groups to the locations suggested in Fig. 1. These proposed structures have not been definitely established, as yet, particularly with reference to the location of some of the polar groups. This fact must be borne in mind throughout the following discussion, as to cite all the possibilities at each reference to structure is not practicable.

2. Apparatus and Procedure

The apparatus is essentially the same as that described by Harkins and Fischer[2] and modified

by Harkins, Carman and Ries.[3] The improved method of determining "zero" or clean surface potentials as described by Harkins, Ries and Carman[1] has been used throughout these experiments.
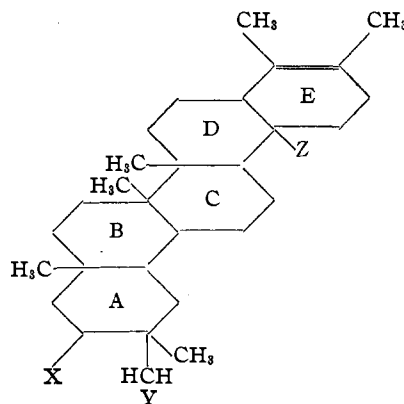

Fig. 1.—General structure of the five-ring compounds.

A modification in the older technique was made to obtain certain effects important in this investigation. As the area of the film was decreased, the torsion wire was turned simultaneously with the movement of the compression barrier. The pressure thus remained balanced during compression and instantaneous pressure readings were obtained. The compression barrier was moved at intervals of one minute and pressure readings taken immediately (unbroken lines) and then thirty seconds later (dotted lines; Figs. 4–6).

The compounds were dissolved in twice distilled chloroform and the films spread on 0.01 molal aqueous hydrochloric acid. The experiments were conducted at room temperature (24–29°) in a metal box covered with a thermal insulation.

3. Pressure–Area Relations

The pressure–area relations for these compounds are shown in Figs. 3–9 and Table I. The condensed films of these substances are of the solid type similar to those of stearic acid. This was demonstrated by the immobility of particles of lycopodium powder on their surface under a jet of air.

(1) Harkins, Ries and Carman, THIS JOURNAL, 57, 2224 (1935).

(2) Harkins and Fischer, J. Chem. Phys., 1, 852 (1933).

(3) Harkins, Carman and Ries, ibid., 3, 692 (1935).

β-Amyrine, 5

Betuline, 7

Betuline diacetate, 2
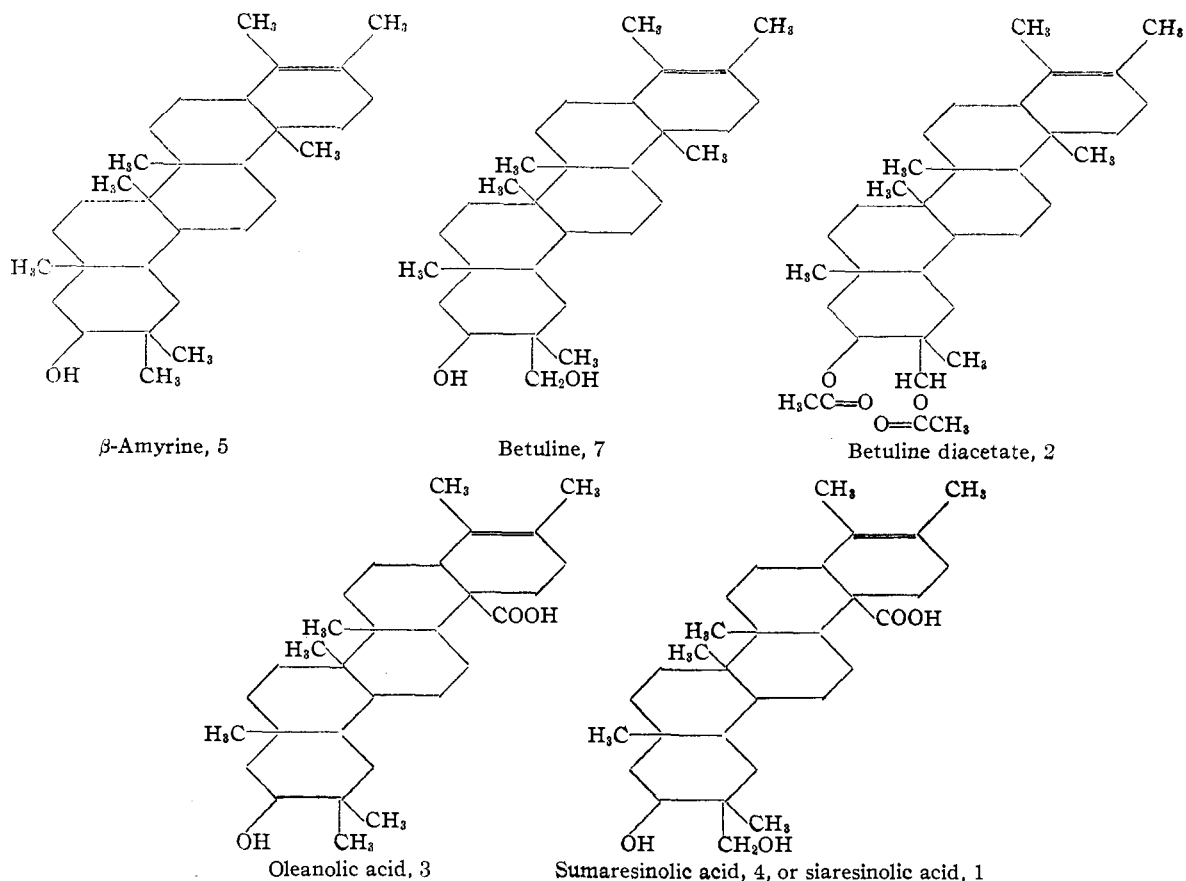
Fig. 2.—Structure of the five-ring compounds (the numbers refer to numbers on the figures).

Oleanolic acid, 3

Sumaresinolic acid, 4, or siaresinolic acid, 1
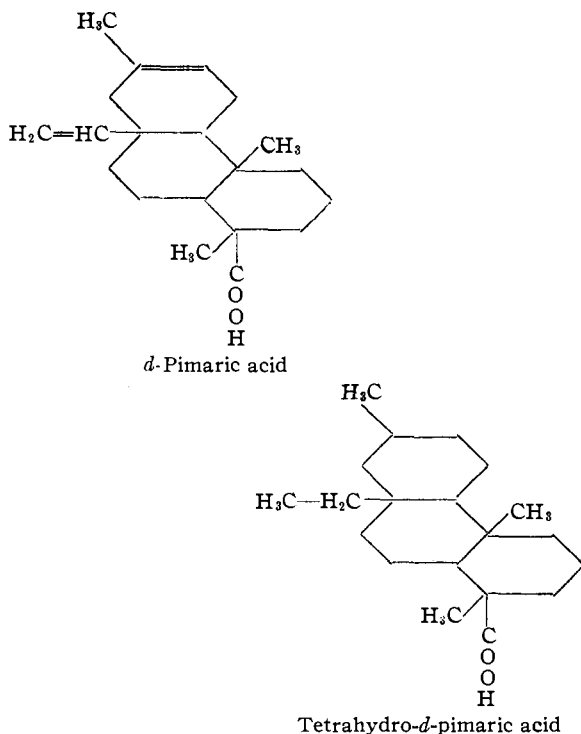
d-Pimaric acid

Tetrahydro-d-pimaric acid

Fig. 3.—Structure of the pimaric acids.

The compressibility coefficients $\dfrac{(a_0 - a_1/a_0)}{f_1 - f_0}$, given in Table I are calculated from the slopes of the curves at pressures just below those of collapse. These coefficients range from 0.0033 to 0.0103 (stearic acid = 0.00763), and are normal for solid condensed films with perpendicular orientation of the molecules. The compressibility coefficient for tetrahydro d-pimaric acid, which has a three-ring structure, is greater than for any of the five-ring compounds, except betuline diacetate. This was to be expected, as pointed out by Harkins, Carman and Ries,[3] since the compressibility of films of vertically oriented molecules decreases with increasing length while that of horizontally oriented molecules is independent of the length. In betuline diacetate the high compressibility is related to the presence of the ester groups.

It may be noted here that at the lower portion of the curves, especially in the case of oleanolic, sumaresinolic and siaresinolic acids, each of which is supposed to contain a carboxyl group at Z in the upper part of the molecule (Fig. 1), the compressibility coefficients are very much larger.

TABLE I

PRESSURE–AREA RELATIONS OF MONOMOLECULAR FILMS OF POLYCYCLIC COMPOUNDS OF THE FIVE-RING SERIES

INITIAL NON-CONTRACTED FILMS

Compounds	Mol. wt.	Den-sity	Vol. of mol-ecule, cu. Å.	Area per molecule at a film pressure			Max. press. fm	t = Film thickness of film at a film pressure			Compressi-bility at $f=0$
				$f=\theta$	$f=10$	$f=$max.		$f=0$	$f=10$	$f=$max.	
β-Amyrine	426.4	0.92	765	46.8	45.2	43.4	22.0	16.3	16.9	17.6	0.0033
Betuline	442.4	.92	792	37.2	37.4	26.4	49.8	21.3	21.2	(30.0)	.0059
Betuline diacetate	526.4	1.0	868	52.6	Collapse	47.6	9.2	16.5	Collapse	18.2	.0103
Oleanolic acid	456.4	0.94	801	55.4	56.6	43.0	47.8	14.5	14.1	18.6	.0047
Sumaresinolic acid	472.4	.92	846	51.0	51.0	43.0	44.8	16.6	16.6	19.7	.0035
Siaresinolic acid	472.4	.94	828	49.0	49.4	37.5	48.0	16.9	16.8	22.8	.0049
Tetrahydro-d-pimaric acid	306.3	1.0	506	52.3	48.8	47.1	14.7	9.70	10.4	10.7	.0068

CONTRACTED FILMS

Contracted curve											
β-Amyrine	See initial values										
Betuline				24.1	26.2	22.0	44.0	32.8	30.2	36.0	0.00198
Betuline diacetate	See initial values										
Oleanolic acid				47.2	47.0	43.0	29.6	17.0	17.1	18.6	.0030
Sumaresinolic acid				51.8	47.8	39.8	24.0	16.3	17.7	21.2	.00965
Siaresinolic acid				42.2	42.6	35.8	33.6	19.6	19.4	23.1	.0045
Tetrahydro-d-pimaric acid	See initial values										

It is interesting to compare the extrapolated areas per molecule at the collapse pressure. The areas for β-amyrine, oleanolic acid and sumaresinolic acid are approximately 43 sq. Å. Betuline gives a much smaller area of about 26 sq. Å. while tetrahydro-d-pimaric acid and betuline diacetate give larger areas of about 47 and 48 sq. Å., respectively.

There seems to be some relation between collapse pressure and the number and kind of polar groups in the molecule. Tetrahydro-d-pimaric acid with three rings and one carboxyl group has a collapse pressure of about 15.0 dynes per cm.; β-amyrine, which contains one hydroxyl group at X and a double bond in ring E has a higher collapse pressure of about 22 dynes per cm. Betuline, oleanolic acid and siaresinolic acid have collapse pressures of about 48 dynes per cm. while that of sumaresinolic acid is about 45 dynes per cm. All of these compounds which exhibit collapse pressures only slightly below 50 dynes, have either two or three polar groups beside the double bond in ring E (Fig. 1). The fact that the adhesion of the film for the substratum is greatly increased in these latter compounds is undoubtedly related to the addition of polar groups to the molecule. By com-

paring betuline with betuline diacetate the effect of changing from two hydroxyl to two acetyl groups is very clearly shown in their collapse pressures. Betuline has a collapse pressure of about 48 dynes
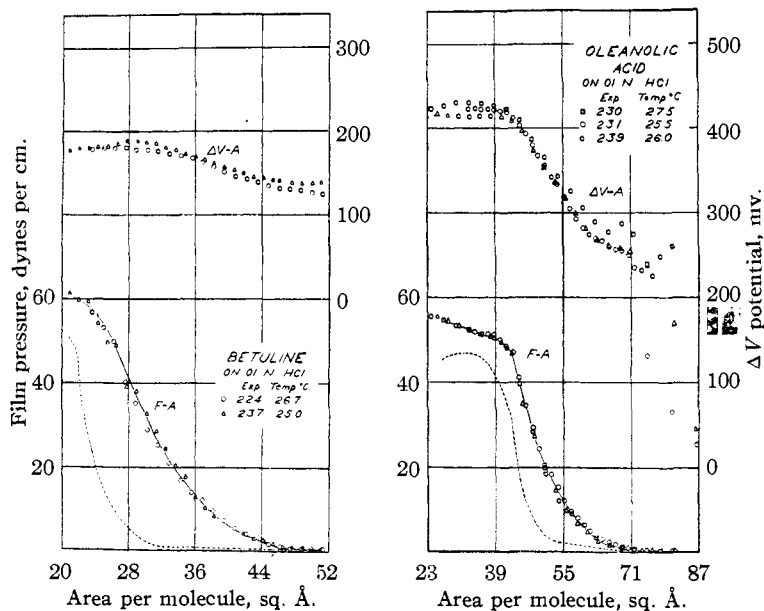
Fig. 4.

per cm. while that of betuline diacetate is only 9 dynes per cm. This illustrates the effect of changing from a strongly to a weakly polar group.

4. Molecular Rearrangement in the Films

It has been pointed out in the introduction that films of betuline exhibit a rapid rearrangement of

the molecules such that the initial pressure, developed during a compression, almost entirely disappears at lower pressures, and largely disappears at higher pressures.

resinolic acid at high but not at low pressures, and appears with films of β-amyrine and of betuline diacetate only at the higher pressures (Figs. 4–6).

Fig. 5.

Thus the phenomenon of molecular readjustment and the resultant shrinkage of the film is very pronounced for those molecules of the five-ring type which have two highly polar groups attached to a single ring. These should be oriented toward the water. The removal of one of these groups, as in β-amyrine, or a change from hydroxyl to acetate groups, as in betuline diacetate, causes the phenomenon nearly to disappear. However, with β-amyrine on 0.02 molar hydrochloric acid Askew[4] found a marked contraction of the film up to an initial pressure of 15 dynes per cm.

When the pressure of a film of betuline was adjusted to 16 dynes every five minutes the area decreased in an hour by 18%, but at 1.0 dyne the decrease in area was only 4.5%. If the pressure
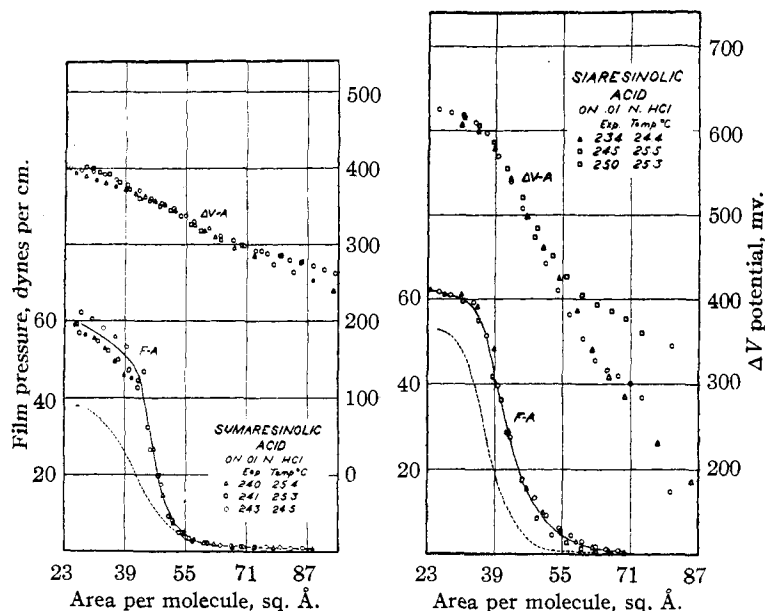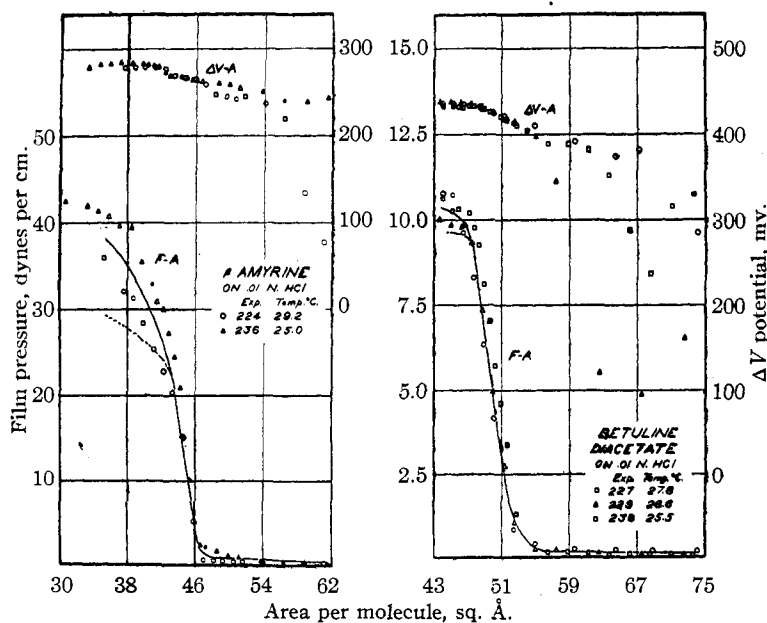
After a compression, the film shrinks for about thirty seconds, but the total decrease in area is small. If now the area is restored to its former larger value by the extremely small expansion necessary, the pressure is greatly reduced, as from 30 dynes to 1 dyne, or from 40 dynes to 5.5 dynes. The film is now under a lower pressure, and does not under this lower pressure undergo any further contraction in five minutes. However, if the pressure is kept at the higher value (as 40 dynes) for five minutes, and the area restored to the initial value at the end of five minutes, the pressure is found to be slightly lower than if the pressure had been reduced by adjusting the area at the end of thirty seconds.

Thus the rate of contraction of the film is higher at high than at low pressures. The shrinkage of the film produces a lowering of pressure, when the area is enlarged to the initial value, which is most extreme for betuline, is also great for oleanolic and siaresinolic acids, is large for suma-

is kept constant at 16 dynes, the decrease in area occurs more rapidly.

Fig. 6.

(4) Askew, Biochem. J., 29, 472 (1935).

5. Molecular Dimensions and Orientation

Models of the five-ring compounds give a value of about 15 Å. as the length of the molecule, and indicate that the molecular area in a tightly packed film, without water present, should be of the order of 50 sq. Å. The values found at 8 dynes per cm. pressure are of this general order (Table I), with the exception of those for betuline, which seems to give a thickness of film which is anomalous, especially at the highest pressure (48.8 dynes/cm.). This indicates either that the film of this particular substance is not truly mono-molecular, or that a part of the betuline has dis-solved.

For the three-ring compound the model gives a molecular length of 10 Å., while the apparent film thicknesses are 9.7, 10.2 and 10.7; at zero (extrapolated), 8, and 14.7 dynes/cm., respec-tively.

These compounds are apparently oriented with the XY ring toward the water, and the presence of a carboxyl group at Z seems to increase the cohe-sion in the film.

6. Surface Potential Relations

The surface potential (ΔV) of a film composed of molecules of an organic substance is the differ-ence between the contact potential of the aqueous surface and that of the surface when covered by the film. This is defined as positive when of the usual sign.

The data for the contact potentials of the six five-ring compounds are represented by the points of Figs. 4–6. As usual, the spread of the points at low pressures is due to non-homogeneity of the film: that is, islands of condensed film and the adjacent gaseous film are represented. In this region the highest values give the surface poten-tial for the islands.

The shrinkage of the film produces very little effect upon the surface potential, so the data refer to either state.

The mean values for the surface potentials of the condensed films are given in Fig. 7. The sur-face potentials increase as the concentration in the film increases, that is, as the molecular area decreases, and most rapidly in the case of siaresin-olic acid, though almost as rapidly for oleanolic acid.

The values of ΔV per molecule are represented by the values of m, where

$$m = \Delta V/n$$

in Fig. 8. Here n is the number of molecules in one sq. cm. of film. The values of $\mu = m/4\pi$ are also given in order to simplify a comparison with the results expressed by English workers. They assume that μ is the dipole moment of the molecules in the film, even although its values are commonly only one-tenth as large as the true di-pole moments. It is recommended that the use of μ be discontinued, since it is the standard symbol for the dipole moment. The equation which has been used for the calculation of μ, is

$$\mu = \Delta V/4\pi n$$

This equation represents a parallel plate condenser with metallic plates, but with the dielectric con-stant (K) omitted. Even for this simple case the correct equation is $\Delta V = 4\pi\sigma d/K$ which they would write $\mu = \Delta VK/4\pi n$.
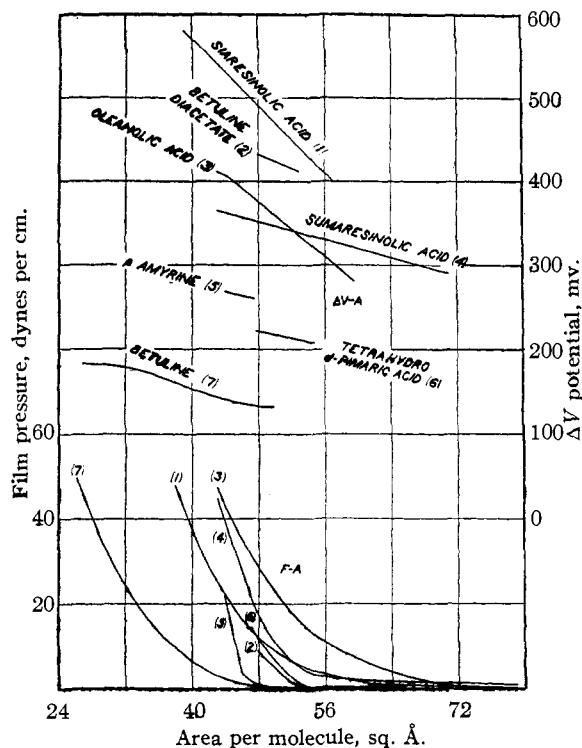

Fig. 7.

If an equation for a condenser could be applied to the case of a film, which is somewhat improb-able, the value of μ would depend upon at least three dielectric constants, and the correct con-stant would not be 4π. It is preferable to use the value of m, which does not assume that the rela-tion to the molecular dipole moments is known.

However, as a preliminary assumption it may be considered that the dipole moments of the molecules of the film contribute to the surface po-

tential, although other factors are involved. It is apparent that the surface potential divided by the number of molecules (m) usually decreases slightly as the number of molecules per unit area increases. That is, though the surface potential (ΔV) increases with the concentration in the film, usually the contribution of each molecule to
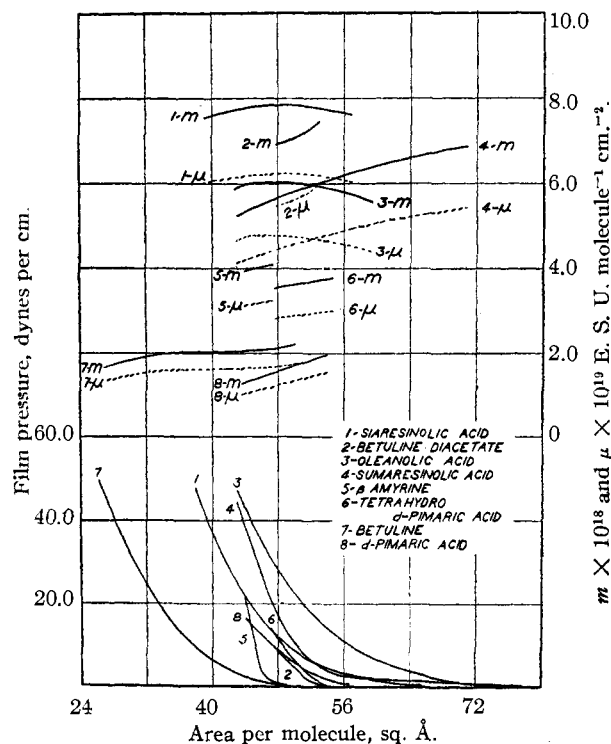

Fig. 8.

ΔV decreases with the concentration. With siaresinolic and oleanolic acids the variations are more complicated.

These relations are presented in a slightly different way in Table II, which gives the percentage increase in surface density and the corresponding percentage increase of surface potential for a specified range of surface density for the condensed film.

In general, the increase of surface density is more than sufficient to account for the increase of surface potential, but with oleanolic and siaresinolic acid the percentage increase of density is less than that of the potential.

Oleanolic acid is β-amyrine in which a hydrogen atom at Z is replaced by a carboxyl group. While with both compounds the surface potential for the condensed film is about 250 mv., the values for oleanolic acid rise to 415 mv. at 39 Å., while at the same molecular area for amyrine the surface

potential is only 280 mv. Thus, when the molecules are closely packed the carboxyl group at Z increases the surface potential by 135 mv. or by about 50%.

The substitution of a hydroxyl group in one of the lower methyl groups (Y) of oleanolic acid to give siaresinolic acid increases the surface potential at low areas from 415 to 625 mv. However, a substitution of a hydroxyl group in the same position in β-amyrine to give betuline lowers the potential by 100 mv. Thus, exactly the same substitution at Y increases the potential by 200 mv. if the carboxyl group is present at Z, and lowers it by 100 mv. if it is not present.

Sumaresinolic acid, which is a stereoisomer of siaresinolic acid, shows widely different surface potential effects. Its potential range, 290 to 400 mv., is considerably lower than that of its isomer (400 to 625 mv.), and is fairly close to that of oleanolic acid, 280 to 430 mv. There is obviously a compensation of the polar groups in the sumaresinolic acid molecule, practically amounting to the complete neutralization of the hydroxyl (Y) group. The striking feature of its potential curve, however, is that the percentage increase of the potential is only 6.67% as compared with its surface density increase of 16.8%. The compensating effect of the dipoles evidently increases rapidly on compression.

The most pronounced compensating effect of the type discussed for sumaresinolic acid was observed for d-pimaric acid, by Harkins, Ries and Carman.[1] As shown in Table II, the surface density increases 16.8% while the surface poten-

TABLE II

THE VARIATION OF SURFACE POTENTIAL WITH SURFACE DENSITY

Compound	Surface potential range, total	Increase of surface density, %	Increase of surface potential, %
β-Amyrine	260–285	16.8	7.44
Betuline	130–190	16.8	14.7
Betuline diacetate	410–440	16.8	8.00
Oleanolic acid	280–430	16.8	21.3
Sumaresinolic acid	290–400	16.8	6.67
Siaresinolic acid	400–625	16.8	19.5
Tetrahydro-d-pimaric acid	205–225	16.8	8.8
d-Pimaric acid	110–80	16.8	−14.1

The percentage changes are calculated from the straight portions of the $\Delta V - A$ curves, not over the total range, thus the change of surface density of 16.8% corresponds to a decrease of area from 56 to 48 sq. Å. for each compound, except for betuline (40 to 34.3) and β-amyrine (48 to 41.1), since for these two compounds the $\Delta V - A$ curves were not linear in the region between 56 and 48 sq. Å.

tial decreases 14.1% though the saturated compound, tetrahydro-d-pimaric acid (one polar group), exhibits normal potential relations.

As mentioned above the magnitude of the potentials of β-amyrine and betuline indicates an electrically oppositional alignment of the two hydroxyl groups in the latter molecule. It is not uncommon for a second polar group to cause a lowering of the surface potential. Similar results were found by us for d-pimaric acid as mentioned above and by others for certain sterols.[5] However, too much weight should not be placed on this relationship in the particular case of betuline, since both its $F-A$ and $V-A$ curves are somewhat anomalous.

The high potential, 410–440 mv., of the comparatively weak film of betuline diacetate is of interest. The addition of the two acetate groups to the betuline molecule has apparently produced marked changes in the film.

The surface potentials of the condensed films vary over a large range, from 130 mv. for betuline to 630 mv. as the maximum for siaresinolic acid.

Summary

The solid monomolecular films of four of the six five-ring compounds considered in this paper have been found to give a behavior not previously exhibited, at least not in anything like this high degree. That is, if kept at constant area the pressure almost entirely disappears due to a shrinkage of the film. The behavior is more nearly analogous to that of a wax than to a crystalline solid. Thus for these films the initial pressure seems to be of much more significance than

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

the final pressure. The initial pressures of all of the films and the surface potentials, are exhibited in Fig. 7, while the final pressures and the potentials are given in Fig. 9.
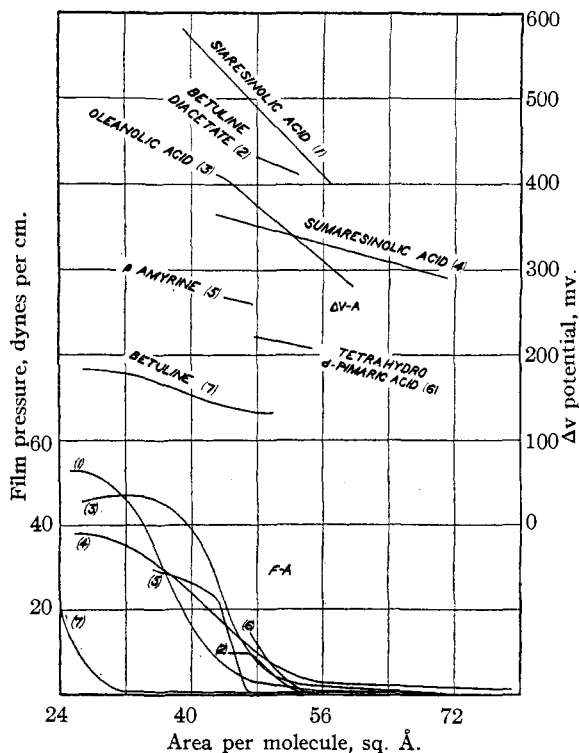

Fig. 9.

At film pressures of eight dynes per cm. the apparent thickness of the film varies from 14 to 17 Å. for the various compounds, which is about the thickness to be expected if molecules with five rings stand on end.

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