

A Surface-balance Study of the Structural Relationships between Cryptopimaric, Dextropimaric, and Isodextropimaric Acids

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In a surface-balance study of monomolecular layers of rosin acids carried out by one of us in 1953¹, it was found that in a compressed monolayer a molecule of dextropimaric acid at 2.5° occupied an area approximately 1.6 Å² larger than that taken up by an isodextropimaric acid molecule. Since, according to the opinion held at that time, these acids were believed to differ from each other only in the steric orientation of the vinyl and methyl groups at carbon-7²⁻⁴*, the observed difference in molecular area was taken to justify certain conclusions about the configurations at this position in the two acids. The configuration that may be expected to occupy the larger area in the monolayer and which can be established by reference to molecular models was that in which the vinyl group is quasi-axially, and the methyl group quasi-equatorially, oriented. This configuration must thus be ascribed to dextropimaric acid and the opposite configuration to isodextropimaric acid¹. During recent years, however, convincing evi-

dence has been collected which indicates that the acids also differ in configuration at carbon-13⁸⁻¹². The true C-7 epimer of dextropimaric acid seems to be cryptopimaric acid^{11,12}, an acid first described in 1937¹³. These new developments, which are illustrated in Fig. 1, do not invalidate the conclusions drawn in Fig. 1, do not invalidate the conclusions drawn about the orientation of the groups at carbon-atom 7 in dextro- and isodextropimaric acids, since the molecular areas taken up by the isodextropimaric-acid molecules with the old and new configurations cannot be expected to differ appreciably. Molecular models of the structures in Fig. 1 are shown in Fig. 2. In view of the importance of the structure of cryptopimaric acid when determining the structural relationships of the pimaric acids, it was considered desirable to supplement the previous monolayer data with similar data for cryptopimaric acid. Through the courtesy of Prof. H. Imamura of Tokyo in providing us with a sample of cryptopimaric acid, we have been able to measure the monolayer characteristics of the acid. At the same time we have repeated the measurements on the other two pimaric acids, using pure samples obtained from Dr. R. V. Lawrence, Olustee, Florida.

The surface-balance pressure-area curves of the three pimaric acids were recorded under identical conditions, and are reproduced in Fig. 3. The monolayers are seen to be similar in their mechanical properties (they are typical liquid condensed monolayers), and in all cases the monolayer collapses at approximately the same surface pressure, *viz.* 19–20 dyn/cm. The areas (Å²) per molecule at the collapse point are:

	3°	20°
Dextropimaric acid	42.4	42.9
Isodextropimaric acid	39.2	40.5
Cryptopimaric	39.2	41.0

* See also Refs. 5-7

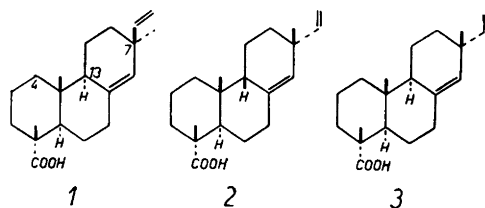


Fig. 1. Structures of 1 dextropimaric, 2 isodextropimaric and 3 cryptopimaric acids (see text).

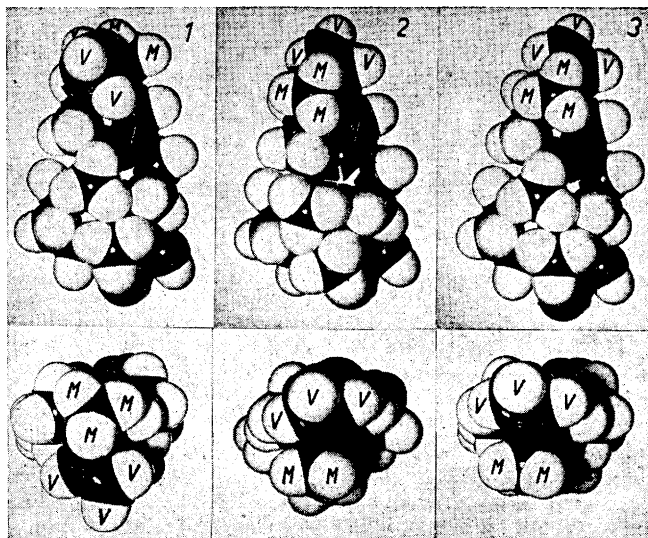


Fig. 2. Molecular models of 1 dextropimaric, 2 isodextropimaric and 3 cryptopimaric acids based on the structures shown in Fig. 1. Upper row, viewed from the front. Lower row, viewed from above. The vinyl and methyl groups at C-7 are indicated by V and M, respectively.

The molecular areas taken up by crypto- and isodextropimaric acid at 3° and 20° are not appreciably different, but they are 2–3 Å² smaller than the areas taken up by dextropimaric acid. These results confirm the previous findings that dextropimaric acid requires a distinctly greater area than isodextropimaric acid in compressed monolayers¹.

The monolayer measurements suggest that cryptopimaric and isodextropimaric

acid both possess the same configuration at C-7, *i.e.* they have a quasi-equatorial vinyl group and a quasi-axial methyl group. This is in agreement with recent infra-red data¹², which have shown that the vinyl group has a different orientation in dextropimaric acid than in crypto- and isodextropimaric acids.

Some of the area values found in the present study are slightly lower than those reported in the earlier study¹. This is

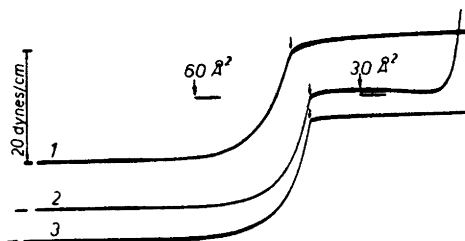


Fig. 3. Surface-balance (pressure-area) curves of 1 dextropimaric, 2 isodextropimaric, and 3 cryptopimaric acids. Substrate, 3 M NaCl, pH 2 (HCl). Temperature, 3.0°C. The points from which the collapse areas were read are indicated by small arrows.

probably not due to the different type of surface balance used (for comparative data obtained with the Wilhelmy-Dervichian and the Mikrokator surface-balances, see Ref.¹⁵), but due to the fact that the samples of rosin acids used in the present study had been purified by chromatography and were exceptionally pure.

In contrast to the pressure-area curves for the other pimaric acids, the curve for isodextropimaric acid exhibits an ascending part due to a relatively rapid solidification of the film under further compression after the collapse of the monolayer (Fig. 3). For further details relating to this interesting phenomenon, which is obviously related to some peculiarity in the structure of the isodextropimaric acid molecule, see Ref.¹⁶

Experimental part. The pressure-area curves were obtained with the recording Mikrokator Balance¹⁴. The rate of compression was approximately 2 cm/min. The substrate was a solution of 3 M sodium chloride (Merek, pro analysi, ignited) brought to pH 2 by addition of hydrochloric acid. The importance of these conditions, which reduce the solubilities of the acid monolayers and the tendency of the monolayers to undergo collapse, has been demonstrated earlier¹. The area values were reproducible within $\pm 0.2 \text{ \AA}^2$. Spreading from benzene and from light petroleum (b.p. 60–80°) gave identical results.

For the physical properties of the rosin acids studied, the reader is referred to Ref.¹¹

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Isolation of Polynuclear Aromatic Hydrocarbons from the Roots of *Chrysanthemum vulgare* Bernh.

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During the investigation of the roots of tansy (*Chrysanthemum vulgare* Bernh.) for the presence of acetylenic compounds¹, one sample collected in the vicinity of the local Gas Works gave a small hydrocarbon fraction with a characteristic ultraviolet spectrum and strong fluorescence, which turned out to be a complex mixture of polynuclear aromatic hydrocarbons.

15 kg of fresh roots were extracted with acetone, and the extracted lipids transferred to light petroleum. From the petroleum soluble material a mixture of sparingly soluble compounds were removed by crystallisation from ether at -10°C . The mother liquor was evaporated to dryness and the residue dissolved in a minimum of hot methanol. This was added to a hot saturated solution of trinitrotoluene in methanol. A yellow crystalline precipitate was formed immediately, and the crystallisation was completed by cooling to -10°C . The mixture of addition compounds was dissolved in benzene and filtered through a

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