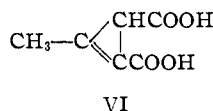
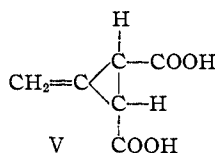
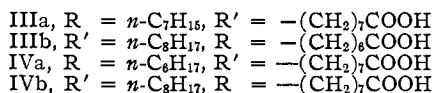
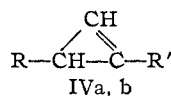
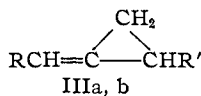
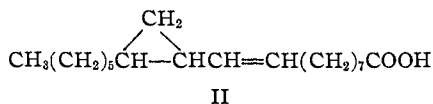
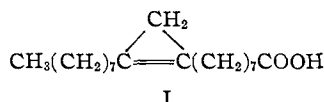


STERCULIC ACID: NUCLEAR MAGNETIC RESONANCE SPECTRUM AND STRUCTURE

Sir:

In light of recent interest<sup>1-7</sup> in the structure of sterculic acid,<sup>1</sup> we wish to present here nuclear magnetic resonance data which allow its definitive formulation as 2-*n*-octyl-1-cyclopropenecaprylic acid (I).

Previous evidence for structure I for sterculic acid includes ozonolysis of the isolated acid to 9,11-diketetonadecanoic acid,<sup>1,2</sup> which has been synthesized,<sup>3</sup> and its hydrogenation to *cis*-9,10-methyleneoctadecanoic acid (dihydrosterculic acid),<sup>1,4,6b</sup> which also has been synthesized.<sup>5</sup>



Other workers, however, have criticized formula I and have proposed the alternative formula II.<sup>6a-c</sup> A more reasonable alternative might be IIIa or IIIb, with the double bond exocyclic to the cyclopropane ring, or, possibly, IVa or IVb, with the double bond in the ring but trisubstituted. These formulas place the cyclopropane ring at the same (correct<sup>6</sup>) position as I but differ from I in the double bond location. Either IIIa or IIIb has the additional advantage of analogy in that ozonolysis of Feist's acid, V, with a double bond exocyclic to a

cyclopropane ring,<sup>8,9</sup> gives no formaldehyde, but principally products expected from the endocyclic olefinic structure VI.<sup>10</sup>

All alternative formulations (II, IIIa, IIIb, IVa, IVb) differ from I in that each of the others has at least one olefinic hydrogen atom, while I has none. The nuclear magnetic resonance spectrum of a compound of formula II, IIIa, IIIb, IVa or IVb would show a peak in the olefinic absorption region ( $\delta$  near 0, H<sub>2</sub>O reference),<sup>8,11</sup> while I would not.

In the present study, sterculic acid, m.p. 19.3-19.9° [lit. m.p. 18.2°,<sup>1,2</sup> 19°<sup>6b</sup>], has been isolated by the procedure of Nunn<sup>1</sup> from the seeds of *Sterculia foetida*. Its infrared spectrum contains a band at 1010 cm.<sup>-1</sup>,<sup>2,6b,7</sup> none at 1642 cm.<sup>-1</sup>,<sup>2,6b</sup> The nuclear magnetic resonance spectrum of the purified acid is given in Fig. 1. Assigned proton absorption<sup>12</sup> is -COOH,  $\delta$  + 6.88; chain -CH<sub>2</sub>-

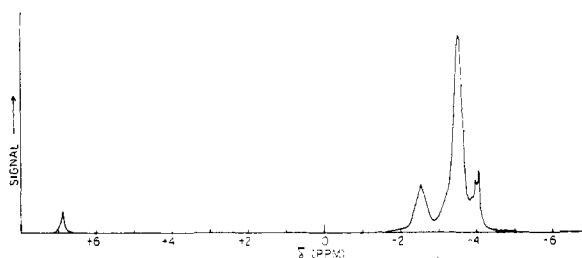
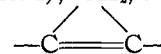


Fig. 1.—Nuclear magnetic resonance spectrum of sterculic acid, determined on pure liquid at room temperature and 40 mc. with Varian Associates High Resolution Spectrometer, 12-in. magnet with Super Stabilizer. Zero of reference scale was water absorption.  $\delta = 10^6 \times (H_r - H)/H_r$ .

$\delta$  -3.50; CH<sub>3</sub>-,  $\delta$  -3.95, -3.85 (split); -CH<sub>2</sub>- adjacent to carboxyl or olefin,  $\delta$  -2.53 (unresolved, integrated intensity of 6-7 protons); CH<sub>2</sub>,  $\delta$  -4.03.



Most significant, there is no peak near  $\delta$  0.00, the region expected for absorption by an olefinic proton (oleic acid<sup>12</sup>  $\delta$  +0.35, elaidic acid<sup>12</sup>  $\delta$  +0.40, Feist's acid diethyl ester<sup>8a</sup>  $\delta$  +0.50, Feist's acid<sup>8c</sup>  $\delta$  ca. +0.62).

The absence of a peak in this region excludes the alternative formulas II, IIIa, IIIb, IVa and IVb, and the present physical evidence, coupled with the syntheses of dihydrosterculic acid<sup>5</sup> and 9,11-diketetonadecanoic acid,<sup>3</sup> allows the unequivocal assignment of formula I to sterculic acid.

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**Acknowledgments.**—We wish to express our appreciation to Dr. W. D. Phillips, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, for determination and interpretation of nuclear magnetic resonance spectra of earlier less highly purified samples of sterculic acid, and to Dr. J. C. Martin of this laboratory for assistance with the determination of the present spectra. We also wish to thank Mr. Hans R. Schmidt of S. B. Penick and Company, for the generous gift of *Sterculia foetida* seeds.

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RECEIVED NOVEMBER 11, 1957

MECHANISM OF SUBSTITUTION REACTIONS OF COMPLEX IONS. XV. ACID AND BASE HYDROLYSIS OF CIS- AND TRANS-DICHLORO-BIS-(ETHYLENE-DIAMINE)-CHROMIUM(III) ION.<sup>1</sup>

Sir:

The rates of acid hydrolysis of chloro complexes of chromium(III) are always greater than those of the corresponding complexes of cobalt(III).<sup>2</sup> This is as expected on the basis of crystal field theory<sup>3</sup> since cobalt(III), with six electrons in the stable  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals, will resist changes in the octahedral arrangement of ligands more strongly than chromium(III) with only three electrons in these orbitals. We recently have measured the rates of both acid and basic hydrolysis for *cis* and *trans*-Cr(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>. The results together with those<sup>4</sup> for *cis* and *trans* Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> are

RATE CONSTANTS AT 25° IN WATER

	$k_{acid}$ , sec. <sup>-1</sup>	$k_{base}$ , M. <sup>-1</sup> sec. <sup>-1</sup>
<i>cis</i> -Cr(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	$3.5 \times 10^{-4}$	$2.7 \times 10^{-2}$
<i>trans</i> -Cr(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	$3.9 \times 10^{-5}$	$3.7 \times 10^{-2}$
<i>cis</i> -Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	$2.5 \times 10^{-4}$	$1.0 \times 10^3$
<i>trans</i> -Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	$3.2 \times 10^{-5}$	$3.0 \times 10^3$

The remarkable result is that the rates of base hydrolysis are about 1/10<sup>5</sup> slower for chromium(III) than for cobalt(III). This demonstrates, at the very least, that a common mechanism is not operating throughout. The slower reaction with hydroxide ion for chromium compared to cobalt is not compatible with an S<sub>N</sub>2 mechanism on either the basis of crystal field or valence bond theory.

The result is explicable on the basis of an S<sub>N</sub>1CB mechanism as previously postulated.<sup>4</sup> The acidities of corresponding chromium and cobalt complexes, where measurable, are found to be about equal.<sup>5</sup> Hence the conjugate bases are formed with about equal ease from either Cr(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> or Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>. The great reactivity of the conjugate base has been ascribed to repulsive  $\pi$ -type interaction between the filled p orbitals of nitrogen in the amido group

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and the filled  $d_{xy}$  type orbitals on the metal atom.<sup>6</sup> This repulsion provides a driving force for loss of chloride ion accompanied by a rearrangement to a trigonal bipyramid intermediate which allows an attractive  $\pi$ -type interaction with the now empty  $d_{x^2-y^2}$  orbital.

It is obvious that chromium with only half as many electrons in the  $d_{xy}$  type orbitals will not supply as much driving force for this process. Hence the over-all much lower rate of release of chloride ion in the presence of alkali can be understood. A similar explanation will hold for *cis*-Co(en)<sub>2</sub>NO<sub>2</sub>Cl<sup>+</sup>, which also reacts very slowly with hydroxide ion.<sup>7</sup> In this case  $\pi$ -bonding from the metal atom to the nitro group reduces the electron occupancy of the  $d_{xy}$  type orbital.

The rates of chloride ion release were measured both in acid and in alkali by amperometric titration of chloride ion. The concentration of complex ion was  $2.00 \times 10^{-3}$  M. Ionic strength was maintained at 0.10 by NaNO<sub>3</sub>. Rates in alkali were measured in a series of solutions containing up to 0.10 M hydroxide ion. The pseudo first order rate constant was found from the experimental half-life for one chloride ion. A plot of rate constant vs. hydroxide ion concentration was linear. From the slope, the second order rate constant given in the table was calculated. The rate constants for acid hydrolysis were found directly in 0.1 M nitric acid and also in acetate-acetic acid buffers of pH 4.2 to 4.6 containing 0.1 M acetate ion. The same rates were obtained in the two media showing that there was no direct reaction with acetate ion. The rate constant for acid hydrolysis could also be found from the intercept of the above mentioned plot. The intercept was equal to about twice the directly measured value, since in alkaline solution the intermediate Cr(en)<sub>2</sub>OHC<sup>+</sup> would rapidly lose the second chloride ion.<sup>8</sup>

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(9) National Science Foundation Pre-doctoral Fellow.

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RECEIVED DECEMBER 6, 1957

A NEW CYCLOPROPYL CORRELATION IN THE NEAR-INFRARED REGION

Sir:

During a recent investigation of certain cyclopropyl derivatives in the near-infrared region of 1.1–2.7 microns, we have noted that in every case of nine derivatives examined, an absorption band has occurred at 1.63–1.65 microns and another at 2.22–2.27 microns.

The spectra were determined using a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. All compounds were run as 10% solutions in carbon tetrachloride in a 3.0 mm. fixed thickness sodium chloride cell. Wave length was calibrated using chloroform and benzene.