which stimulates the rate of cellulose digestion *in vitro* has been reported from this laboratory.[1] We now wish to report that a volatile fraction from acidified rumen juice and various straight and branched chain fatty acids have cellulolytic factor activity for rumen microörganisms *in vitro*.

The addition of centrifuged rumen juice to a medium composed of mineral salts, purified wood cellulose, biotin, *p*-aminobenzoic acid and glucose inoculated with rumen microörganisms obtained by supercentrifugation of strained rumen juice increased cellulose digestion from 19% as observed in the unsupplemented flask to 58% during a 30-hour fermentation (see Table I). When the distillates obtained by ordinary distillation from rumen juice were added to the medium, the distillates from the acidified rumen juice (*p*H 2.0 to 2.5) with H_3PO_4 were active whereas distillates from juice made alkaline (*p*H 10 to 11) with NaOH prior to distillation were inactive. When the material remaining in the distillation flasks was neutralized and added to the fermentation flasks, the alkaline residue was active while there was little activity left in the acid residue.

TABLE I

Additions to basal medium	Expts.	Av. cellulose digested, % pct.
None	13	19.2
Centrifuged rumen juice (CR J)	13	58.2
Dist. from *p*H 2–2.5 CR J	6	53.3
Res. from acid dist. CR J	3	16.3
Dist. from *p*H 10–11 CR J	4	18.2
Res. from alk. dist. CR J	4	61.1
n-Valeric acid[a]	8	56.3
Iso-valeric acid	1	38.6
Iso-butyric acid	1	38.7
Caproic acid	3	49.5
Valine	8	38.5
Proline	3	36.3
Valine plus proline	1	55.7

[a] Acids and amino acids added at level of 0.004 to 0.01%.

The behavior of the active material to distillation suggests that this substance(s) is a steam volatile fatty acid. The addition of short-chained volatile fatty acids to the fermentation medium increased cellulose digestion. Caproic and *n*-valeric acids were the most active although iso-valeric and isobutyric acids were found to have some stimulatory effect. Acetic, propionic and butyric acids, the normal end products of cellulose digestion by rumen microörganisms, were inactive as were samples of C_7 to C_{10} straight chain fatty acids tested.

The occurrence of five-carbon acids in animal fat has been reported recently.[2] Valeric acid as well as branched chain five-carbon acids have been isolated from rumen juice[3] as rumen microörganisms form these acids from amino acids and proteins.[4]

Besides the volatile component obtained from rumen juice which would appear to be one or more of the volatile fatty acids tested above, there appears to be additional non-volatile cellulolytic factor(s) which are responsible for the factor activity found in certain feeds and yeast or yeast by-products. This factor may be related to the amino acid content of these feedstuffs. Preliminary evidence now available indicates that α-amino homologs of the volatile fatty acids used in this study are also active.

The activity of these fatty acids or their amino acid precursors is not restricted entirely to cellulose digestion. The conversion of urea nitrogen into trichloroacetic acid precipitable protein is also increased.

DEPARTMENT OF ANIMAL SCIENCE
OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER, OHIO

ORVILLE G. BENTLEY
ALFRED LEHMKUHL
RONALD R. JOHNSON
T. V. HERSHBERGER
A. L. MOXON

RECEIVED AUGUST 31, 1954

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[1] O. G. Bentley, R. R. Johnson, S. Vanecko and C. H. Hunt, *J. An. Sci.*, **13**, 581 (1954).

[2] R. P. Hansen and A. G. McInnes, *Nature*, **173**, 1093 (1954).

[3] E. F. Annison, *Biochem. J.*, **57**, 400 (1954).

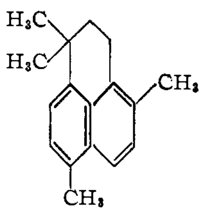
[4] K. El-Shazly, *ibid.*, **51**, 640 (1952).

THE STRUCTURE OF CATIVIC ACID

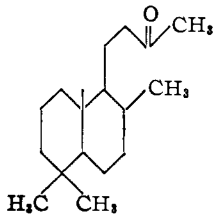
Sir:

"Cativo," an oleoresinous exudate of *Prioria capaifera*, Griseb., was found by Kalman[1] to consist of an easily esterifiable, unsaturated acid, $C_{20}H_{34}O_2$, and a neutral fraction which was assumed to be the corresponding ester, cativyl cativate. We wish to report now the complete structure of this diterpenic acid.

Cativic acid, m.p. 80–82°,[2] $[\alpha]^{26}\text{D}$ −6.54° (EtOH) [*Anal.* Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; neut. equiv., 303. Found: C, 78.22; H, 10.92; 306] was dehydrogenated with palladium-charcoal to **1,2,5,6-tetramethylnaphthalene,** m.p. 114.5–115°; **picrate,** m.p. 151–153°; **trinitrobenzolate,** m.p. 180–181°.[3] These constants as well as the ultraviolet and infrared spectra are closely comparable to those of an authentic sample of this hydrocarbon and its reported derivatives. Dehydrogenation experiments with selenium at 325° led to a $C_{17}H_{20}$ hydrocarbon as major product, identical in all respects to that obtained by a similar dehydrogenation of agathic acid[4] and, by way of infrared spectra comparison, to **1,1,4,7-tetramethylphenalan** (I), recently synthesized by Büchi and Pappas[5]: m.p. 39–40.5°; **picrate,** m.p. 136–138°; **styphnate,** m.p. 153–155°.



I



II

Cativic acid, on catalytic hydrogenation, absorbed one mole equivalent of hydrogen and, after Fischer esterification, yielded methyl dihydrocativate, m.p. 43–44°, $[\alpha]^{27}\text{D}$ +23.4°. This ester was

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[1] N. V. Kalman, THIS JOURNAL, **60**, 1423 (1938).

[2] Kalman's acid was non-crystalline due to isomeric inhomogeneity. The isomerization of cativic acid will be discussed in a future paper.

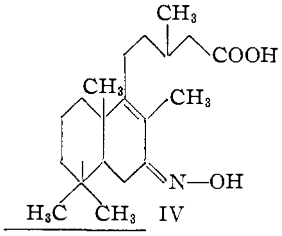
[3] E. Lederer, *et al.*, *Helv. Chim. Acta*, **29**, 1354 (1946), also have isolated this anomalous product from the Pd-C dehydrogenation of ambreinolide.

[4] L. Ruzicka and J. R. Hosking, *ibid.*, **13**, 1402 (1930).

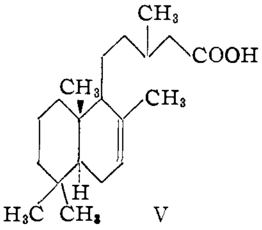
[5] G. Büchi and J. J. Pappas, THIS JOURNAL, **76**, 2963 (1954).

subjected to a two-step Barbier–Wieland degradation from whence a methyl ketone was derived, whose **semicarbazone** (III), m.p. 201.5–202°, $[\alpha]^{31}_{D}$ +66.6° ($CHCl_3$), was found to have the same constants and infrared spectrum as that derivative of the methyl ketone (II) arising from the degradation of manoöl.[6] Repetition of this degradation yielded a semicarbazone which melted undepressed with III and had a specific rotation of +65.4°. Stereochemically and structurally, therefore, cativic acid is related to the dicyclic diterpenes.

Cativic acid contains one element of unsaturation (perbenzoic acid titration) which must lie in the ring system, for no carbon atoms were lost when the acid was ozonized. Furthermore, the ozonolysis product gave a positive iodoform reaction, from which test the inference was drawn that C-6 was one of the double bond terminals. Although manoöl and agathic acid have exocyclic unsaturation, the ozonization and infrared data on cativic acid allowed the elimination of this possibility. Methyl cativate (from diazomethane esterification of the acid), n^{25}_{D} 1.4954, $[\alpha]^{30}_{D}$ −7.51°, when reacted with amyl nitrite and concentrated hydrochloric acid in chloroform at −30° and then warmed to room temperature over a total time of about 10 minutes, was converted directly to the α,β-unsaturated oxime (IV),[7] m.p. 121.5–122°, λ_{max} 246 mμ (log ϵ 4.01); λ (—C=C—C=N—OH) 6.17 μ. *Anal.* Calcd. for $C_{21}H_{35}O_3N$: C, 72.16; H, 10.09; N, 4.01. Found: C, 71.97; H, 10.31; N, 4.24. This evidence permits the complete structure of cativic acid to be written as V.



IV



V

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[6] J. R. Hosking and C. W. Brandt, *Ber.*, **68**, 1311 (1935).

[7] Another example of this reaction is the conversion of α-pinene to nitrosopinene by boiling pinene nitrosochloride in carbon tetrachloride for two minutes: J. C. Earl and J. Kenner, *J. Chem. Soc.*, 1269 (1927).

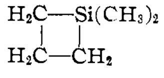
CONTRIBUTION NO. 1245 FROM
STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT
FREDERICK W. GRANT, JR.
HAROLD H. ZEISS

RECEIVED AUGUST 16, 1954

A SILICON-CONTAINING 4-RING

Sir:

We wish to record the synthesis of a highly strained silicon heterocycle with silicon as the hetero atom, 1,1-dimethyl-1-silacyclobutane, compound I.



$$\begin{array}{l} \mathrm{H_2C—Si(CH_3)_2} \\ \;\;| \qquad | \\ \mathrm{H_2C—CH_2} \end{array}$$

I

On the assumption that the silacyclobutane ring is planar and that the C–C–C angle is tetrahedral (at least to a first approximation) calculation using 1.94 Å. for C–Si and 1.54 Å. for C–C bond lengths 80°48′ for the C–Si–C bond angle and 84°52′ for each of the two C–C–Si bond angles.[1]

The reaction sequence used for the synthesis of compound I was

$$\mathrm{Me_3Si(CH_2)_3Br} \xrightarrow[\text{(2) }\mathrm{H_2O}]{\text{(1) }\mathrm{H_2SO_4}} [\mathrm{Br(CH_2)_3SiMe_2}]_2\mathrm{O} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{NH_4Cl}}$$

$$\mathrm{Br(CH_2)_3SiMe_2Cl} \xrightarrow[\mathrm{Et_2O}]{\mathrm{Mg}} \mathrm{(CH_2)_3SiMe_2}$$

Ring closure in dilute ether solution gave a 66% yield of the silacyclobutane, b. p. 81° (730 mm.,) n^{20}_{D} 1.4270, d^{20} 0.7746, MR_D 33.2 (calcd., 32.8); *Anal.* Calcd. for $C_5H_{12}Si$: Si, 28.0; C, 60.0; mol. wt., 100.2. Found: Si, 28.0; C, 60.3; mol. wt., 98. An infrared spectrum showed no Si—H band and no maximum for C=C.

Chemical effects of the strain at the silicon atom are quite interesting. Preliminary experiments showed that compound I gives a highly exothermic reaction with 1 *N* potassium hydroxide in ethyl alcohol merely on mixing at room temperature. In further contrast to ordinary tetraalkylsilanes the silacyclobutane reacts violently with concentrated sulfuric acid at room temperature despite the heterogeneous nature of the reaction. The above reactions proceed without gas evolution and thus involve ring-opening.

Further proof of structure was afforded by treatment of the silacyclobutane with concentrated sulfuric acid at 0°. Ring-opening followed by hydrolysis of the reaction product gave as the expected product di-*n*-propyltetramethyldisiloxane, identical with an authentic sample prepared from hydrolysis of the product obtained from dimethyldiethoxysilane and *n*-propylmagnesium bromide, b. p. 182° (730 mm.), n^{20}_{D} 1.4088, MR_D 67.4 (calcd., 67.4). *Anal.* Calcd. for $C_{10}H_{26}SiO_2$: Si, 25.8. Found: Si, 25.9.

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[1] Given a nearly planar structure for the silacyclobutane ring, it follows that the C–Si–C angle cannot be greatly increased without expansion of the C–C–C angle beyond the tetrahedral value. For small deviation from planarity in perfluorocyclobutane see H. P. Lenaire and R. L. Livingston, THIS JOURNAL, **74**, 5732 (1952).

DEPARTMENT OF CHEMISTRY
COLLEGE OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE UNIVERSITY
STATE COLLEGE, PA.
LEO H. SOMMER
GERALD A. BAUM

RECEIVED JULY 22, 1954

ISOCITRITASE: A NEW TRICARBOXYLIC ACID CLEAVAGE SYSTEM

Sir:

Campbell, Smith and Eagles[1] reported the formation of glyoxylic acid from citric and *cis*-aconitic acids by crude extracts of *Pseudomonas aeruginosa*. The pertinence of this observation arises from its indication of a new enzyme system for the cleavage of tricarboxylic acids, and in the formation of glyoxylic acid, a biosynthetic precursor of glycine[2] and of active C_1.[3]

By the use of sonic extracts of this pseudomonad, fractionated to remove aconitase, we have shown

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[1] J. J. R. Campbell, R. A. Smith and B. A. Eagles, *Biochim. et Biophys. Acta*, **11**, 594 (1953).

[2] S. Weinhouse and B. Friedmann, *J. Biol. Chem.*, **191**, 707 (1951).

[3] S. Weinhouse and B. Friedmann, *ibid.*, **197**, 733 (1952).