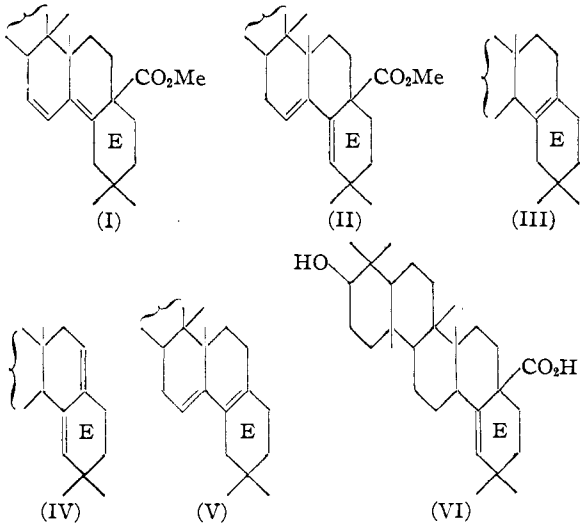
COMMUNICATIONS TO THE EDITOR

MOROLIC ACID, A TRITERPENOID SAPOGENIN

Sir:

A recent communication[1] reported the isolation from the heart-wood of *Mora excelsa* Benth. of a saponin, which furnished a crystalline sapogenin on hydrolysis. Through the courtesy of Mr. Campbell and Dr. Farmer, who kindly provided us with generous supplies of raw material, we have been able to elucidate the constitution of the sapogenin. The latter is a new triterpenoid hydroxycarboxylic acid $C_{30}H_{48}O_3$, and we propose for it the name morolic acid. Morolic acid, m. p. 273° dec. $[\alpha]_D$ +31°[2] (acetate, m. p. 256–257°, $[\alpha]_D$ +44°, equivalent 498) was converted to the acetate methyl ester, m. p. 263–264°, $[\alpha]_D$ +38°, which was reduced by lithium aluminum hydride to the corresponding glycol, $C_{30}H_{50}O_2$, m. p. 220°, $[\alpha]_D$ −11° (diacetate, m. p. 273°, $[\alpha]_D$ +23°). The latter contains one secondary and one primary hydroxyl group. By standard reactions the $-CH_2OH$ grouping was converted to $-CH_3$. In this way the known triterpenoid alcohol germanicol, $C_{30}H_{50}O$, resulted.[3]



Morolic acid acetate methyl ester readily furnished a saturated oxide (*Anal.* Calcd. for $C_{33}H_{52}O_5$: C, 74.96; H, 9.91. Found: C, 74.96; H, 9.86) which on treatment with hydrogen chloride in dry chloroform afforded dehydroöleanolic acid acetate methyl ester.[4] Oxidation of morolic acid acetate methyl ester by selenium dioxide, or fission of the oxide with ethanolic sulfuric acid, afforded the methyl ester, m. p. 188°, $[\alpha]_D$ +214°, $\lambda_{max.}$ (EtOH) 237 mμ; ε, 10,200, of a new acid. On isomerization by hydrogen chloride in chloroform the acetate methyl ester of this acid furnished the above-mentioned dehydroöleanolic acid acetate methyl ester. The latter is now to be formulated as (I), the former as (II).

On melting morolic acid was quantitatively converted to oleanol, now formulated as (III), the same easy decarboxylation to the same product being observed with *o*-oleanolic acid.[5] Reduction of morolic acid acetate methyl ester oxide by lithium aluminum hydride, followed by acetylation, gave the conjugated nor-diene acetate (IV), m. p., 220–222°, $[\alpha]_D$ −19°, $\lambda_{max.}$ (EtOH) 240 mμ; ε, 17, 100 (*Anal.* Calcd. for $C_{31}H_{48}O_2$: C, 82.06; H, 10.66. Found: C, 81.92; H, 10.78), the constitution of which has been confirmed by an unambiguous synthesis based on siaresinolic acid. (IV) was also obtained by the action of perbenzoic acid on morolic acid acetate. Isomerization afforded the nor-diene acetate (V), m. p. 189–190°, $[\alpha]_D$ +68°, $\lambda_{max.}$ (EtOH) 244 mμ; ε, 18,800, the constitution of which was proved by its formation by the facile decarboxylation of the acid corresponding to (II).

These experiments provide evidence that morolic acid has the constitution (VI).

We are indebted to Sir John Simonsen, F. R. S., and Professor E. R. H. Jones, F. R. S., for their interest in this work.

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(1) Farmer and Campbell, *Nature*, **165**, 237 (1950).

(2) M. p.'s are uncorrected; all rotations were determined in chloroform.

(3) Simpson, *J. Chem. Soc.*, 283 (1944); we are indebted to Dr. Simpson for an authentic specimen.

(4) Ruzicka, Grob and van der Sluys-Veer, *Helv. Chim. Acta*, **22**, 788 (1939).

(5) Compare Jeger, Norymberski and Ruzicka, *Helv. Chim. Acta*, **27**, 1533 (1944).

(6) Harvard University Visiting Lecturer, 1949–1950.

THE OPTICAL ROTATION OF PEPTIDES

Sir:

The optical rotation of peptides may be considered an additive function of the contributions of the asymmetric carbon atoms of the constituent amino acid residues (R).[1] The rotation of an amino acid residue, $S_1 \ldots [R] \ldots S_2$ is taken as $[\alpha] \times R/100$, where $[\alpha]$ is the specific rotation, R the residue weight, S_1 and S_2 residue substituents.[2] For dipeptides containing glycine, residue rotations are obtained by multiplying the specific rotation of the peptide with its residue weight. For other dipeptides, residue rotations are calculated by adding or subtracting the specific rotations of a pair of analogous peptides (L–L and L–D (or D–L))

(1) The first three letters of amino acids are used for R in "typical" peptides (Ala, Gly, Lys) (*cf.* E. Brand, *Ann. N. Y. Acad. Sci.*, **47**, 187 (1946)).

(2) Only the state NH_3^+,COOH is considered throughout.

and multiplying with the average residue weight of the peptide. Such calculations[3] are based on the assumption that the contributions of a D-residue and of an L-residue are numerically the same but opposite in sign.

From the specific rotations of some peptides (Table I) the residue rotations (Table II) were calculated.

TABLE I

SPECIFIC ROTATIONS[a] OF ALANINE[b] AND LYSINE PEPTIDES[c]

(1)	H·Ala-Gly·OH(L);	$[\alpha]^{24}$ + 13.8°
(2)	H·Gly-Ala·OH(L);	$[\alpha]^{24}$ −52.9°
(3)	H·Ala-Ala·OH(L-L);	$[\alpha]^{26}$ −38.3°
(4)	H·Ala-Ala·OH(L-D);	$[\alpha]^{24}$ +67.2°
(5)	H·Gly-Ala-Ala·OH(L-L);	$[\alpha]^{23}$ −87.9°
(6)	H·Gly-Ala-Ala·OH(L-D);	$[\alpha]^{23}$ −14.0°
(7)	H·Lys-Gly·OH(L);	$[\alpha]^{24}$ +31.1°
(8)	H·Gly-Lys·OH(L);	$[\alpha]^{25}$ −9.0°
(9)	H·Ala-Lys·OH(L-L);	$[\alpha]^{25}$ −7.2°
(10)	H·Ala-Lys·OH(D-L);	$[\alpha]^{25}$ −27.9°
(11)	H·Lys-Ala·OH(L-L);	$[\alpha]^{25}$ −1.9°
(12)	H·Lys-Ala·OH(L-D);	$[\alpha]^{26}$ +70.9°
(13)	H·Lys-Lys·OH(L-L);	$[\alpha]^{25}$ +5.6°
(14)	H·Lys-Lys·OH(L-D);	$[\alpha]^{23}$ +39.6°

[a] To ensure the state NH_3^+,COOH for ionizable groups, all rotations (λ = D; t = 23–26°; c = 2) were determined within five minutes after dissolving in 6 *N* hydrochloric acid. Rotations were constant for half an hour. [b] In part gift from Dr. Jesse P. Greenstein. [c] Peptides (1) to (4) and (7) are known (*cf.* J. S. Fruton, *Adv. Prot. Chem.*, **5**, 1 (1949)); the others were synthesized by the carbobenzoxy–azide method (the satisfactory analytical data are omitted).

TABLE II

RESIDUE ROTATIONS OF L-ALANINE AND L-LYSINE RESIDUES

H...[Ala]...Gly·OH	+18°	H·Gly...[Ala]...OH	−68°
H...[Ala]...Ala·OH	+21°	H·Ala...[Ala]...OH	−75°
		H·Gly-Ala...[Ala]...OH	−74°
H...[Ala]...Lys·OH	+21°	H·Lys...[Ala]...OH	−73°
H·Gly...[Ala]...Ala·OH	−102°		
H...[Lys]...Gly·OH	+58°	H·Gly...[Lys]...OH	−17°
H...[Lys]...Ala·OH	+69°	H·Ala...[Lys]...OH	−35°
H...[Lys]...Lys·OH	+58°	H·Lys...[Lys]...OH	−44°

Apparently L-alanine and L-lysine residues are dextrorotatory in "amide" substitution (amino end), levorotatory in "acyl" substitution (carboxyl end) and as "acyl amide" (endo position).[4]

Detailed interpretation of the relatively uniform values for alanine and of the drift in the lysine values must await the investigation of additional peptides. This should also lead to a clearer understanding of the optical rotation of peptides and may prove valuable in the determination of amino acid sequences.

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(3) *Cf.* C. S. Hudson, THIS JOURNAL, **39**, 66 (1909). While this work was in progress, M. A. Nyman and R. M. Herbst, *J. Org. Chem.*, **15**, 108 (1950), have published the calculation of the contributions of the asymmetric carbon atoms of leucine dipeptides.

(4) For poly L-lysine, H·Lys-(Lys-)$_{28}$-Lys·OH, we find $[\alpha]^{23}$ −79.3°.

THE EXCHANGE REACTION BETWEEN FERROUS AND FERRIC IONS IN PERCHLORIC ACID SOLUTIONS[1]

Sir:

It has been variously reported that the electron transfer exchange reaction between ferrous and ferric ions, is fast,[2] very slow[3] or complete within one to two hours.[4] Some of the discrepancies in past work have been attributed to catalysis of the exchange reaction during the chemical separation employed to separate the exchanging species. However, Linnenbom and Wahl[4] were unable to confirm the result of Van Alten and Rice[3] that separation by a diffusion method permitted observation of a very slow exchange.

In an attempt to resolve these discrepancies a quantitative chemical separation has been devised which leads to only a small amount of induced exchange. The results to date indicate that the reaction is indeed a rapid one but that its rate can be measured. The separation is based on formation of the very stable complex between α,α'-dipyridyl and ferrous ion. Solutions of the reactants are mixed with rapid and continued stirring, and at the desired time the reaction is quenched by adding in rapid succession an excess of a dilute solution of dipyridyl followed by sufficient sodium acetate solution to bring the *p*H to about 5. Subsequently, the ferric iron is precipitated by addition of ammonium hydroxide. The iron in either or both fractions is finally converted to ferric 8-hydroxyquinolate and counted as such. The tracer used in the experiments here reported was Fe^{55}, obtained from Oak Ridge and was initially in the ferric species.

Figure 1 shows the data for one of the runs. The reaction appears well behaved and exhibits the usual exponential time dependence. A sum-

TABLE I

HALF-TIME OF THE FERROUS–FERRIC EXCHANGE REACTION UNDER VARIOUS CONDITIONS

$HClO_4$ formal	Formal $Fe^{+++} \times 10^{-3}$	$Fe^{++} \times 10^{-3}$	Chloride formal	Half-time, sec.
0.4	0.83	1.06	Trace, *ca.* 10^{-5}	23 ± 2
.4	1.00	1.10	Undetect. 10^{-6} or less	20 ± 2
.4	1.00	1.10	Undetect. 10^{-6} or less	18 ± 3
.4	1.00	1.10	0.8×10^{-3} added	21 ± 2
.4	0.50	0.55	Undetect.	44 ± 4
3.0	1.00	1.10	Undetect.	15 ± 4

(1) Research carried out at Brookhaven National Laboratory under the auspices of the Atomic Energy Commission.

(2) P. Nahinsky, Ph.D. Thesis, Univ. of Calif., 1942.

(3) L. Van Alten and C. N. Rice, THIS JOURNAL, **70**, 883 (1948).

(4) V. J. Linnenbom and A. C. Wahl, *ibid.*, **71**, 2589 (1939).