shown as the points on the left-hand abscissa in the figure. When small amounts of the D-residues are present the rotation is seen to increase linearly. Extrapolation of these data to the composition of a racemic mixture permits the estimation of the specific rotation of a right-handed helix free of any residue contribution. This estimated value is +48° for $[\alpha]_D$ and +105° for the residue rotation. The latter figure is the value that should be compared with the prediction of +68° by Fitts and Kirkwood[4] instead of the differences between the rotations of helical and randomly coiled configurations which has been employed. The agreement is well within the uncertainties of the two figures. The value recently published for polyleucine[10] is 31% higher than that reported here.

It has been pointed out that the steric hindrance between β-carbon atoms may be sufficient to prevent or weaken the α-helical configuration when both D and L residues are present. The copolymers used for the above measurements provide an opportunity to test this suggestion by making use of the transition that can be observed when the ratio of a solvent favoring the helical configuration to one favoring the random coil configuration is gradually changed. The sharpness of this transition and its similarities to a melting process have been discussed already.[2] This transition is conveniently detected by measuring the rotation as dichloroacetic acid is added to a chlororform solution of the polypeptide.[12] The results of this kind of experiment are shown in the figure. The pure L-polypeptide helix "melts out" sharply at about 68% dichloroacetic acid. However, with increasing D-residue content the melting out of the helical structure occurs at successively lower dichloroacetic acid concentrations and the range over which the melting occurs is broadened. Since the molecular weights of these polymers were of the same order of magnitude (~100,000) it is clear that the introduction of optical isomers brings about a proportionate weakening of the helix. Inasmuch as the helical configuration of L-polypeptides and proteins possesses only a rather marginal stability in aqueous media[3,12] it is apparent that these structures would not be maintained if significant amounts of D-residues were present.[13]

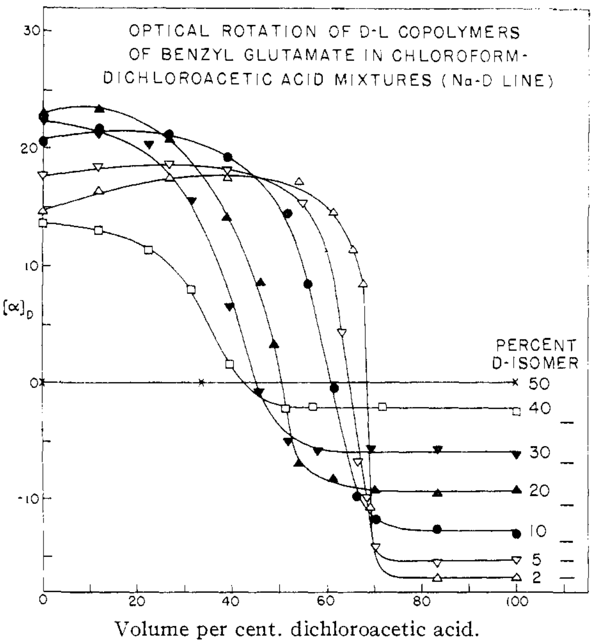

Fig. 1.—The specific rotation (sodium D-line) of poly-γ-benzyl glutamate as a function of the amount of dichloroacetic acid added to chloroform solutions. The lines on the right indicate the rotation expected if rotations of D and L-residues are additive. The data for the pure L-polypeptide ($[\alpha]_D$ 13.8° in $CHCl_3$) have been omitted because they fall so close to the polymer containing 2% D-residues.

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(12) J. T. Yang and P. Doty, THIS JOURNAL, in press.

(13) We wish to acknowledge support of this work by the Office of the Surgeon General, Department of the Army and the Office of Naval Research (N5ori-07654).

(14) Chemical Research Laboratory, Polaroid Corporation, Cambridge 39, Massachusetts.

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THE RING FISSION OF CYCLOPROPANES: THE CONSTITUTION OF MAALIOL

Sir:

Acid catalyzed cleavages of cyclopropanes obey the rule of Markownikoff. In other words, opening occurs between the carbon atoms holding the smallest and largest number of alkyl groups.[1] We now would like to suggest that derivatives of bicyclo[4,1,0]heptane lead to diaxial cyclohexanes or monoaxial cyclohexenes. Such a mechanism accounts readily for the acid catalyzed isomerizations of cycloartenol,[2,3] cyclolaudenol,[4] phyllanthol[2] and carene.[5] In the course of structural studies on maaliol (I), $C_{15}H_{26}O$, m.p. 103–104°,[6] which turns out to be a sequiterpene homolog of carane, we have now observed a non-Markownikoff cleavage of a cyclopropane. On treatment with anhydrous hydrogen chloride at 20° maaliane (II) was transformed to an olefin (IV or VI), b.p. 115° (7 mm.), found: C, 87.39; H, 12.52; 3.33, 6.14, 11.36 μ. Osmylation followed by glycol cleavage with lead tetraacetate gave formaldehyde and a norketone (V or VII), m.p. 33°, found: C, 81.17; H, 11.81; 5.88, μ, *negative* iodoform test, 2.98 *D* introduced with NaOD in EtOD. The operation of the mechanism discussed above for acid cleavage of cyclopropanes is handicapped in this case by the instability of the intermediate (III). Examination of III reveals that such a structure would be unduly strained because of the three bulky *cis*-1,3-triaxial groups. The molecule being a *trans*-decalin cannot undergo ring transformation to the

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(1) R. A. Raphael in E. H. Rodd, "The Chemistry of Carbon Compounds," Vol. IIA, Elsevier, Amsterdam, 1953, p. 26.

(2) D. H. R. Barton, E. W. Warnhoff and J. E. Page, *J. Chem. Soc.*, 2715 (1954).

(3) D. S. Irvine, J. A. Henry and F. S. Spring, *ibid.*, 1316 (1955).

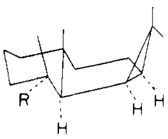
(4) J. A. Henry, D. S. Irvine and F. S. Spring, *ibid.*, 1607 (1955).

(5) Ref. 1, Vol. IIB, p. 558.

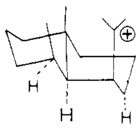
(6) *Schimmel Reports*, 137 (1908).

3e conformation. *It is this conformational effect which is responsible for the non-Markownikoff opening and subsequent Wagner–Meerwein rearrangement actually observed.*[7]

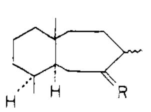
The structure of maaaliol (I) has been deduced from the following degradations: Acetylation of I with ketene gave the acetate (XI), m.p. 36°, found: C, 77.36; H, 10.60. Pyrolysis of XI at 300° produced mainly VIII, b.p. 121° (11 mm), found: C, 87.75; H, 11.72; 3.35 6.11, 11.34 μ. On catalytic hydrogenation of VIII over Pd/C II was formed which did *not* show infrared absorption due to methylene in a cyclopropane.[8] Osmylation of VIII led to a single diol which was oxidized with lead tetraacetate to formaldehyde and a norketone (IX), m.p. 58°, found: C, 81.47; H, 10.82; 5.87 μ, which was stable to base; 2.95 *D* introduced with NaOD in EtOD. Oxidation of IX with perbenzoic acid gave lactone XII, m.p. 113°, found: C, 75.67; H, 9.79; 5.82 μ. The corresponding hydroxycarboxylic acid (XIII), m.p. 120°, found: C, 70.06; H, 10.07, on Sarett oxidation was converted to X, m.p. 64°; 5.85, 5.90, 9.92 μ; λ max. 215 mμ ε 2650. Light absorption of X is characteristic of cyclopropyl ketones.[9] We have established the presence and location of a cyclopropane ring in I by a second sequence to be discussed in the full paper. Dehydrogenation of I over Pd/C at 330° gave eudalene (50%) and vetivalene (1%). The presence of a geminal dimethyl in I was established by destructive oxidation of I with permanganate which led to α-hydroxyisobutyric acid.



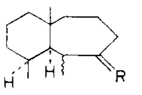
I, R = OH
II, R = H



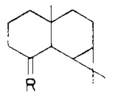
III



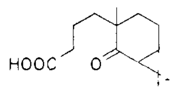
IV, R = CH^2
V, R = O



VI, R = CH_2
VII, R = O



VIII, R = CH_2
IX, R = O



X

The relative configurations of four out of the five asymmetric centers present in I is evident from the facts presented above. The formation of epi-maaliol (XIV); m.p. 59°, found: C, 81.12; H, 11.71 exclusively on treatment of IX with methylmagnesium bromide points to an equatorial hydroxyl in I.

Acknowledgments.—We are indebted to Firmenich and Co., Geneva, for financial support, to the N.I.H. for a fellowship to D. M. W. and to Dr. Alida Hosking-Wind for the maaliol which was made available to us by Prof. O. Jeger, Zürich.

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[7] A similar effect seems to cause the abnormal behavior of aromadendrene (A. J. Birch and F. N. Lahey, *Australian J. Chem.*, **6**, 379 (1953)).

[8] A. R. H. Cole, *J. Chem. Soc.*, 3807, 3810 (1954).

[9] R. H. Eastman and S. K. Freeman, THIS JOURNAL, **77**, 6642 (1955).

A COMPARISON OF THE RADIOLYSIS AND MASS SPECTROMETRY OF SEVERAL DEUTERATED ETHANOLS

Sir:

The formation of acetaldehyde and 2,3-dihydroxybutane during the radiolysis of ethanol with ionizing radiation has been generally attributed to attack on the ethanol molecule at the $-CH_2-$ position.[1] Substantial proof of this mechanism together with a more detailed insight into it has now been obtained by means of the isotopic tracer technique. CD_3CH_2OH, CH_3CD_2OH, CH_3CH_2OD, and C_2D_6O have been prepared by standard methods,[2] and have been irradiated in the liquid phase with Co^{60} gammas to total dosages of about 5×10^{20} e.v. per gram.[3]

The measurements obtained from these irradiations have been (a) the rate of hydrogen (= hydrogen + deuterium) production, expressed as molecules of hydrogen produced per 100 e.v. absorbed ($G(H_2)$), and (b) the deuterium content of the hydrogen so obtained. These data are shown in Table I. In addition, the mass patterns of the first two deutero-ethanols have been obtained in a Nier-type spectrometer; the pertinent portions of these patterns are shown in Table II.

TABLE I

Substance	$G(H_2)$[a]	% Deuterium in radiolytic hydrogen[b]
CH_3CH_2OH	3.66 ± 0.26	. . .
CD_3CH_2OH	3.90 ± 0.15	4.27
CH_3CD_2OH	2.81[c]	42.0
CH_3CH_2OD	3.67 ± 0.08	34.2
CD_3CD_2OD[d]	2.98 ± 0.04	93–95[e]

[a] These are the averages and average deviations obtained from two or three independent irradiations. [b] Mass spectrometer analysis. [c] Single experiment. [d] Sample furnished by Tracerlab, Inc. [e] This low value must reflect contamination or exchange during work-up and analysis.

From the data in Table I, it may be concluded that $G(H_2)$ is lowered from the value observed in ethanol (3.66) to that observed in perdeutero-ethanol (2.98) by deuterium substitution only in the $-CH_2-$ group; $G(H_2)$ is unaffected by deuterium

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[1] *Cf.* for example, W. McDonnell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

[2] The isotopic purity of these materials was 95–100% as measured by examination of the infrared spectra. These purities were confirmed by examination of the mass patterns and the nuclear magnetic resonance lines. The materials were chemically pure within the limits detectable with a Perkin–Elmer Vapor Fractometer. Infrared examination of the recovered, redistilled, irradiated alcohols showed that no randomization of the label had occurred during the irradiation. No exchange between molecular hydrogen and substrate alcohol occurred (*cf.* J. G. Burr, Jr., *J. Chem. Phys.*, **25**, 587 (1956)) under the conditions of these irradiations.

[3] These doses are on the linear portion of the yield curve for hydrogen; *cf.* A. S. Newton and W. McDonnell, THIS JOURNAL, **78**, 4554 (1956).