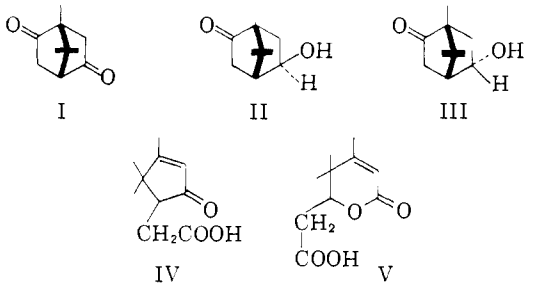
COMMUNICATIONS TO THE EDITOR

MICROBIOLOGICAL DEGRADATION OF (+)-CAMPHOR

Sir:

Clarification of the biosynthesis of complex organic structures, *e.g.*, terpenoids and alkaloids, is proceeding rapidly. In contrast the processes of biodegradation which are intrinsic to the continual redistribution of carbon in Nature generally have been ignored. This paper describes some initial studies on the microbiological decomposition of (+)-camphor.

A pseudomonad, strain P, isolated from sewage sludge by enrichment techniques using (+)-camphor as a carbon source, was grown on a medium containing (+)-camphor (0.5%) and minerals.[1] Extraction of the broths at the end of the logarithmic growth phase and chromatography of the neutral fraction yielded (1) a keto-camphor identified as 2,5-diketocamphane (I) by comparison with an authentic sample,[2] (2) a hydroxyketone, m.p. 220.5–221.5°, $[a]^{EtOH}_D$ + 41° (*c*, 71.48; H, 10.60), identified as 5-*exo*-hydroxycamphor (II)[3] by the physical properties, the correspondence of *p*-nitrobenzoate,[4] 3,5-dinitrobenzoate[5] and semicarbazone[4] derivatives, and oxidation to I,[6] and (3) other hydroxyketones (oxidizable to I) including 5-*endo*-hydroxycamphor (III) isolated as the *p*-nitrobenzoate, m.p. 147–148° (C, 64.45; H, 6.05; N, 4.26), the structure of which was clarified by n.m.r.



The acid fraction afforded a keto acid, $C_{10}H_{14}O_3$, m.p. 104–108°, $[a]^{EtOH}_D$ −57°, $\nu_{max}^{CHCl_3}$ 1705, 1620 cm.$^{-1}$, $\lambda_{max}^{C_2H_5OH}$ 227 mμ(ε, 14,000), (*c*, 65.80; H, 7.92; neut equiv., 183), equilibrated by heating in aqueous solution to a racemate m.p. 125–127°, dihydro derivative, m.p. 83–84°, $\nu_{max}^{CHCl_3}$ 1735, 1710 cm.$^{-1}$ (C, 65.15; H, 9.20). These spectral features together with n.m.r. data on the methyl ester [peak at 0.475[7] from C=CHCO, four methyl peaks at +1.65, +3.30, +4.15 and +4.38 and a 3-proton multiplet at +2.7] suggested structure IV and identity was established by comparison with authentic IV.[8]

Complete oxidation of the acid IV by the resting bacterial cells is inhibited by 2,2′-bipyridine with the accumulation of a new intermediate, $C_{10}H_{14}O_4$, m.p. 105.5–107°, $[a]^{CHCl_3}_D$ +57° (*c*, 60.62; H, 7.16; 32.01; neut. equiv., 201), $\lambda_{max}^{H_2O}$ 220 mμ (ε, 9750). n.m.r. (peaks at −0.45, +0.80 (triplet), +2.58 (doublet), +3.30, +4.15, +4.22) and I.R. ($\nu_{max}^{CHCl_3}$ 1710, 1726 cm.$^{-1}$) spectra indicated structure V. This assignment was confirmed by hydrogenation to a dihydro lactone, m.p. 135–136°, $[a]^{CHCl_3}_D$ −17.5°, infrared and nuclear magnetic resonance spectra identical with the lactone from racemic dihydro IV and peracetic acid, m.p. 129–129.5° (C, 59.97; H, 7.84).

The pathway by which camphor is degraded by this organism can be partially formulated as: (+)-camphor → 5-hydroxycamphor → I → IV → V, a succinct process for the cleavage of both carbocyclic rings.[9]

(1) R. Y. Stanier, M. Doudoroff and E. A. Adelberg, "General Microbiology," The Macmillan Co., New York, N. Y., 1958, p. 286.

(2) J. Bredt and A. Goeb, *J. prakt. Chem.*, **101**, 288 (1921).

(3) See Y. Asahina and M. Ishidate, *Ber.*, **64**, 188 (1931).

(4) M. Ishidate, H. Kawahata and K. Nakazawa, *ibid.*, **74**, 1707 (1941).

(5) F. Reinhartz and W. Zanke, *ibid.*, **67**, 552 (1934).

(6) The configuration at C_5 is assigned from the n.m.r. absorption of the 5-proton which occurs as a triplet in the *p*-nitrobenzoate (5.5 cps. band spacing). See *e.g.*, M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959). See also K. Takeuchi, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **23**, 288 (1933).

(7) Chemical shift in p.p.m. relative to external CH_2Cl_2 in solvent $CDCl_3$.

(8) J. Bredt and P. Pinten, *J. prakt. Chem.*, **119**, 81 (1928); Y. Asahina and M. Ishidate, *Ber.*, **67**, 440 (1934).

(9) Supported in part by the National Science Foundation.

(10) Department of Chemistry, Harvard University, Cambridge, Massachusetts.

(11) Esso Post-Doctoral Fellow, 1958–1959.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

W. H. BRADSHAW
H. E. CONRAD
E. J. COREY[10]
I. C. GUNSALUS
D. LEDNICER[11]

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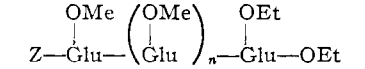
CONFORMATIONAL TRANSITIONS IN POLYPEPTIDES

Sir:

We wish to report the discovery of a conformational transition in low molecular weight polypeptide chains. Optically active peptides of the type



(where *n* is an integer between zero and seven and *Z* is the benzyloxycarbonyl group) have been prepared.[1] The rotations of the compounds were taken in dichloroacetic acid and in dioxane (Fig. 1). In dichloroacetic acid values were negative and decreased, approaching those found for the high molecular weight polymers in this solvent.[2] In dioxane a similar plot was obtained for the di-, tri- and tetrapeptides. However, at the pentamer stage the rotation suddenly shifted to a positive value and continued to rise as the residues increased. For high molecular weight glutamic acid esters positive rotations have been attributed to helical forms.[3]

(1) Details of the synthesis will be published elsewhere. The general method is described in M. Goodman and K. C. Stueben, THIS JOURNAL, **81**, 3980 (1959).

(2) E. R. Blout, R. H. Karlson, P. Doty and B. Hargitay, *ibid.*, **76**, 4492 (1954).

(3) (a) C. Robinson and M. S. Bott, *Nature*, **168**, 325 (1951); (b) P. Doty and J. T. Yang, THIS JOURNAL, **78**, 498 (1956); (c) J. T. Yang and P. Doty, *ibid.*, **79**, 761 (1957); (d) P. Doty and R. D. Lundberg,