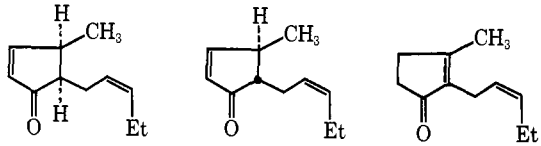
Completion of the cyclopentenone synthesis required a study of optimum conditions for the retro Diels–Alder reaction. In particular, we were interested in defining conditions which would lead cleanly to cyclopentenones of type I, with no migration of the double bond. Of course, if only the rearranged cyclopentenones (*cf.* II) are required, the position of the double bond after cracking, as well as the stereoisomeric composition of the alkylated mixture (*e.g.*, VIIa–VIIb), would both be inconsequential. It was found, after much experimentation, that while atmospheric pressure distillation, or heating in sealed quartz or Pyrex tubes gave mixtures of I and II, *it is possible to obtain pure cyclopentenones of type I in quantitative yields by slow addition of the "adducts"* (*e.g.*, V, VI, VIIa,b) at the top of a quartz column filled with quartz chips and maintained at 600° while the system is kept under ~0.2 mm (the pyrolysate is collected in a Dry Ice cooled flask). In this manner, a number of pure cyclopentenones of type I were obtained, *e.g.*, I (R_1 = H, R_2 = CH_3[8]), I (R_1 = R_2 = CH_3), and I (R_1 = *cis*-2-pentenyl, R_2 = CH_3), free from the isomeric II, as easily shown by nmr; characteristic α and β vinyl protons in I at δ ~6.0 and 7.4–7.5 (1 H each, d of d, $J_{\alpha,\beta}$ = 6 Hz) and doublet due to 4-methyl group at δ ~1.2 (J = 7 Hz) changing in the isomeric II, R_2 = CH_3, to δ 2.1.

Isomerization to the more stable isomer II could be effected in a variety of ways such as heating with acid,[8] or in sealed Pyrex tubes (220°, 1 hr). Aqueous base isomerization is often convenient. Refluxing with 0.5% aqueous potassium hydroxide for 2 hr of either the trans isomer VIIIb (from VIIb) or of the mixture from VIIa,b gave in about 85% yield (~50% overall from V) *cis*-jasmone IX identical (ir, nmr, uv, mass spectrum, vpc) with an authentic sample.[9,10]



VIIIa VIIIb IX

(8) *Cf.* G. W. Cavill, B. S. Goodrich, and D. G. Laing, *Aust. J. Chem.*, 23, 83 (1970).

(9) *Cf., inter alia*, G. Stork and R. Borch, *J. Amer. Chem. Soc.*, 86, 936 (1964).

(10) The group at Columbia wishes to thank the National Science Foundation and the National Institutes of Health for partial support of this work.

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Calorimetric Measurements on the "Normal" Temperature-Induced Helix–Coil Transition of Poly(*N*-γ-carbobenzoxy-L-α,γ-diaminobutyric acid)

Sir:

The enthalpy of the helix-to-coil transition of a number of homo- and copolypeptides in the mixed solvent system dichloroethane–dichloroacetic acid (DCE–DCA) is substantially independent of the nature of the side chains. The process is exothermic and its ΔH value, deduced from calorimetric experiments, is in neighborhood of 600–650 cal/mol of residue.[1-4]

The right-handed helical conformation of all polypeptides studied to date is stabilized in DCA–DCE by increasing the temperature.[5]

Poly(*N*-γ-carbobenzoxy-L-α,γ-diaminobutyric acid) is the only exception.[6] As demonstrated from recent ORD experiments in Yang's laboratory, the temperature-induced helix-to-coil transition of this polypeptide shows "normal" behavior; *i.e.*, its helical state is reached only by lowering the temperature from 30 to about −30°.[7] We have applied the heat of solution calorimetric method[1-3,8] to the study of this system and to its higher homolog poly(*N*-δ-carbobenzoxy-L-ornithine) (PCBO).

First, we have confirmed Yang's results in the solvent system DCA–DCE that we have used in all previous calorimetric experiments. As usual, in the case of PCBO, we observed an "inverted" temperature-induced helix-to-coil transition. At room temperature and 37% (vol) DCA, a high-molecular-weight sample existed as a solvated random coil (b_0 = 0) and, upon heating, a transition to the helix (b_0 = −600 at 75°) occurred between 30 and 75°.

On the other hand, for a high-molecular-weight PCBBA sample,[9] at 55% (vol) DCA, the transition was "normal" and completed within a temperature range larger than that of PCBO. The random-coil conformation at 80° ($b_0 \simeq 0$) was partially changed into helix by lowering the temperature (b_0 = −340 at 30°).

Figure 1 shows the results of the heat of solution measurements. The change of behavior in going from PCBO to PCBBA is dramatic.

The first part of the ΔH_{sol} curve of PCBO (low DCA content) shows the usual saturation trend which we have associated with side-chain solvation by dichloroacetic acid.[2] At higher DCA content, the sharp change of the solution enthalpy value, occurring at the same DCA concentration as the jump in optical activity, is due to the order–disorder heat effect of an exothermic process (650 cal/mol of residue).

On the other hand, the ΔH_{sol} curve of PCBBA at low DCA content shows only a slight linear variation, having, in addition, opposite sign to those of all other polypeptides investigated.

At 40% (vol) DCA, we observe a sudden change in the ΔH_{sol} corresponding to an exothermic process similar to that observed for PCBO, immediately fol-

(1) G. Giacometti in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, London, 1968, pp 67–76.

(2) G. Giacometti, A. Turolla, and R. Boni, *Biopolymers*, 6, 441 (1968).

(3) G. Giacometti, A. Turolla, and R. Boni, *ibid.*, 9, 979 (1970).

(4) A. Kagemoto and R. Fujishiro, *ibid.*, 6, 1753 (1968).

(5) G. D. Fasman in "Poly-α-Amino Acids," G. D. Fasman, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 11.

(6) Another "normal" temperature-induced helix-to-coil transition is that found by Y. Hayashi, *et al.*, *Biopolymers*, 8, 403 (1969), in a study of poly(β-benzyl L-aspartate) in *m*-cresol. In this case, however, the L-polypeptide has a left-handed helical structure.

(7) F. Gaskin, S. Kubota, and J. T. Yang, *J. Amer. Chem. Soc.*, 91, 6526 (1969).

(8) G. Giacometti and A. Turolla, *Z. Phys. Chem.* (*Frankfurt am Main*), 51, 108 (1966).

(9) Details on this synthesis will be reported elsewhere.

lowed by a second endothermic process occurring at 50% (vol) DCA.

An optical titration experiment on this polypeptide in the same solvent mixture and at the same temperature shows no sign of a conformational transition until a 50% (vol) DCA concentration is reached; the collapse of the helix occurs at the same solvent composition as that of the endothermic process.

We interpret the calorimetric results at low DCA content as evidence of the existence of specific hydrogen bonds between the urethane linkages of the carbobenzoxy groups.[10,11]

A side chain–side chain interaction of this sort would explain the much lower affinity of the acid for solvating the side chains.

The exothermic process (600 cal/mol of residue) occurring before 50% (vol) DCA *without a corresponding change in the optical rotation* could be explained only if we accept the possibility of breaking the α-helix hydrogen bonds by DCA solvation and if we further assume that an ordered and DCA-solvated structure of the polypeptide backbone is still maintained with the cooperation of the side-chains hydrogen bonds.

Consequently, the increase of ΔH_{sol} after 50% (vol) DCA, which corresponds to an endothermic process (250–300 cal/mol of residue) and is paralleled by a sharp change in optical activity, could be associated with the disruption of the ordered structure of the backbone by a cooperative breaking of the external hydrogen bonds.

(10) M. Hatano, M. Yoneyama, I. Ito, T. Nozawa, and M. Nakai, *J. Amer. Chem. Soc.*, **91**, 2165 (1969).
(11) M. Hatano and M. Yoneyama, *ibid.*, **92**, 1392 (1970).

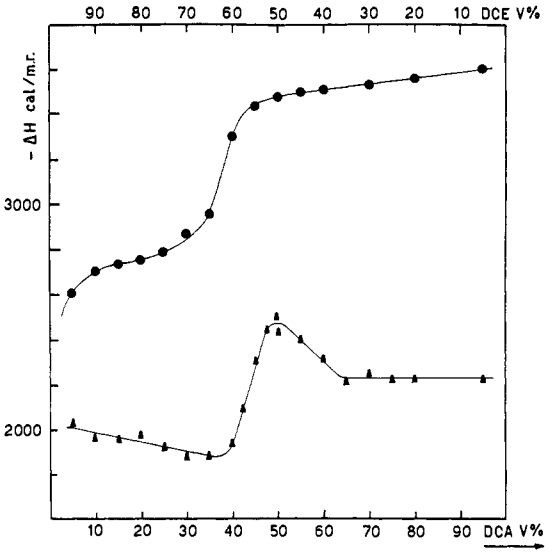

Figure 1. ΔH_{sol} values in DCE–DCA mixtures at 30°: ●, poly(*N*-δ-carbobenzoxy-L-ornithine); ▲, poly(*N*-γ-carbobenzoxy-L-α,γ-diaminobutyric acid). Final polymer concentration always about 2 g/l.

Details on ORD (as well as on nmr) experiments on these polypeptides will be reported elsewhere.

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Book Reviews

Progress in Phytochemistry, Volume 2, Edited by L. RHEINHOLD and Y. LIWSCHITZ (The Hebrew University of Jerusalem, Israel). Interscience Publishers, John Wiley & Sons, Inc., New York, N. Y. 1970. ix + 512 pp. $27.50.

The volume under review contains eight articles of interest written by acknowledged authorities in their respective fields.

The first article, by Barbier, reviews the chemistry and biochemistry of pollens. Numerous pollens are known to contain antibiotics, but not antifungal substances. Methods for the collection of pollens and conditions for pollen germination are described. Available data on the chemical composition of pollen are comprehensively reviewed in areas such as vitamins, enzymes, carbohydrates, pigments, lipids, proteins, amino acids, nucleic acids, sterols, and steroids.

The article by Hatch and Slack examines recent progress toward our understanding of the C_4-dicarboxylic acid pathway of photosynthesis. They present a short history of Calvin's photosynthetic cycle and an account of the events leading to the discovery of the C_4-dicarboxylic acid cycle. The distribution, regulation, and physiological significance of the pathway are also discussed. This article is especially useful for the nonspecialist interested in a general overview of this subject.

The article by Akazawa briefly reviews the history of Fraction I protein, its identity with RuDP carboxylase, and its structure and function. Its kinetic properties and its localization in the cell are also described. Evidence is also presented that other enzymes are also present in Fraction I, and the possibility that Fraction I protein may actually be a multienzyme complex is considered.

The relationships between plants, insects, and isoprenoids are analyzed in the article by Herout. Occurrence and functions of monoterpenes, sesquiterpenes, diterpenes, triterpenes, and steroids are considered as they relate to plane and insect physiology. Various isoprenoids are reported to function as feeding attractants or repellents, or are required by the insect as juvenile hormones or molting hormones.

The chemistry, biosynthesis, and occurrence of the nonprotein amino acids of plants are well reviewed by Fowden. Although most of these compounds have only recently been described, they now number over 200. The comparative phytochemistry of these compounds is examined at the family, tribe, and genus level. There is also a discussion of the possible role of nonprotein amino acids as antimetabolites.

The article by Wallwork and Crane describes the nature and occurrence of plant preylquinones and related compounds such as the ubiquinones, rhodoquinone, tocopherolquinone, tocochromanols, the plastoquinones, and the benzoquinones. The review of the biosynthesis of those quinones is excellent. Localization of quinones in the cell and the effect of nutrition on quinone concentration are discussed briefly. In the treatment of the roles of some of the well-known quinones, emphasis is placed on that of plastoquinone.

Mapson and Hulme describe the *in vivo* and the cell-free synthesis