Anal. Calcd. for $C_6H_6O_4(CNS)_6$: N, 17.14. Found: N, 17.05.[1]

The synthesis of this addition compound of kojic acid was the result of an attempt to prepare the 6-thiocyanokojic acid.

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RECEIVED MARCH 18, 1947

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[1] Analysis by Dr. Carl Tiedcke.

COMMUNICATIONS TO THE EDITOR

INFRARED SPECTRA AND STRUCTURE OF NATURAL AND SYNTHETIC POLYPEPTIDES

Sir:

We wish to report the main features of the infrared spectrum that we have obtained of a synthetic polypeptide recently prepared by Woodward and Schramm.[1] There is a very close resemblance between this spectrum and that of a film of denatured keratin,[2] as can be seen from Fig. 1.

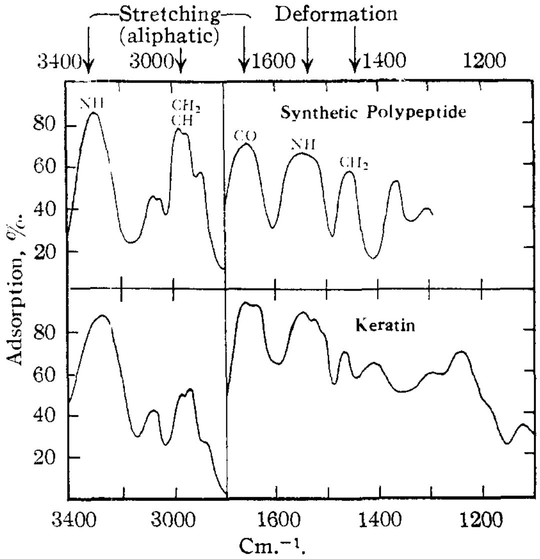

Fig. 1.—Infrared aborption spectra of Woodward and Schramm: synthetic polypeptide, and of keratin, 3400–1100 cm.$^{-1}$.

The interpretation of the principal bands is indicated on the curves. At the high frequency end of the spectrum the strong band at 3300 cm.$^{-1}$ arises from the stretching vibration of the NH bond. Its position and width show that the hydrogen atom is loosely bonded, presumably to the oxygen atom of the C=O group in a neighboring chain. The group of bands between 2970 and 2880 cm.$^{-1}$ arise from stretching vibrations of the CH groups in the methylene group and the "lone" CH of the side chain. The band at 1650 cm.$^{-1}$ arises from the C=O of the peptide link, while that at 1550 cm.$^{-1}$ is due to the deformation vibration of the NH group. The band at 1450 cm.$^{-1}$ is due to a well-known deformation vibration of the CH_2 group. The weak band near 3060 cm.$^{-1}$ is partly due to the CH stretching frequencies of the phenyl group but is also connected either with the NH or the C=O since it is associated with hydrogen with hydrogen bonding effects in simple amides.

The great similarity with the spectrum of keratin is thus fully explained and the fact that differences begin to appear only at frequencies below 1450 cm.$^{-1}$ is just what might be expected since it is in this region that skeletal and other frequencies characteristic of the residues in the polypeptide chain will occur. Indeed this illustrates another very important aspect of the use of these new synthetic polypeptides for by comparison with the spectrum of the parent amino acid it should be possible to identify with certainty the frequencies characterizing the residue of a given amino acid in a protein. We have found that this is not feasible with the smaller polypeptides hitherto available (*e. g.*, leucylglycylglycine) where the end groups still dominate the spectrum.

This work was carried out with the aid of grants from the Medical Research Council and the Wool Industries Research Association, which we gratefully acknowledge.

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RECEIVED JULY 19, 1947

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[1] Woodward and Schramm, THIS JOURNAL, **69**, 1551 (1947). We thank Professor H. Mark for a small sample of this material supplied to him by Professor Woodward.

[2] Kindly supplied by the Wool Industries Research Association.

SYNTHESIS AND STRUCTURE OF TETRAHYDROPYRETHROLONE

Sir:

LaForge and Soloway[1] assigned the α-ketol structure (Ia) to the synthetic hydroxydihydrocinerone not identical with natural *dl*-dihydrocinerolone and proposed the β-ketol structure (IIa) for the other synthetic isomer identical with racemic natural material. Assignment of these structures was based on reinterpretation of earlier experimental evidence and on rational interpretation of the reactions employed, with the belief that N-bromosuccinimide characteristically brominates on the allylic position.[2] N-

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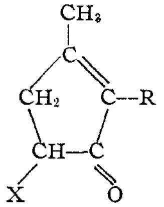
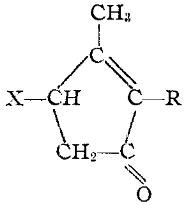
[1] LaForge and Soloway, THIS JOURNAL, **69**, 186, 979 (1947).

[2] Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).

Bromosuccinimide also substitutes bromine on methylene groups *alpha* to carbonyls of saturated cyclic and acyclic ketones[3] and of α,β-unsaturated ketones of the mesityl oxide type[4] but substitutes on the allylic methylene of Δ^4-3-ketosteroids.[5]



Ia, R = *n*-Bu, X = OH
Ib, R = *n*-Am, X = OH



IIa, R = *n*-Bu, X = OH
IIb, R = *n*-Am, X = OH
IIc, R = *n*-Am, X = Br

Prior to publication of the dihydrocinerolone synthesis,[1] we had employed the N-bromosuccinimide reaction for the synthesis of the homologous *dl*-tetrahydropyrethrolone. Its identity with the natural product has now been established and additional evidence obtained to support the contention of allylic bromination and β-ketol structure. The slow reaction of tetrahydropyrethrolone with periodic acid (2.8–3.2% equivalent in forty-eight hours) indicates the absence of an α-ketol structure (Ib),[6] and as a consequence the β-ketol structure (IIb), proposed by LaForge and Soloway,[1] becomes the most likely structure for tetrahydropyrethrolone.

Reaction between equimolar quantities of tetrahydropyrethrone and N-bromosuccinimide in carbon tetrachloride was complete after thirty minutes of heating under reflux. Distillation of the filtered solution gave 67% yield of bromoketone (IIc), b. p. 115–122° (2.2–2.3 mm.), n^{25}D 1.5100, which, on refluxing for four hours with silver acetate in glacial acetic acid, gave *dl*-tetrahydropyrethrolone acetate in 70% yield, b. p. 120–123° (1.0–1.4 mm.), n^{26}D 1.4755 (calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.7; H, 9.24); semicarbazone, m. p. 85–86°; *p*-nitrophenylhydrazone, m. p. 146°. The only constants reported are for the *d*-enantiomorph, b. p. 117° (1.3 mm.), n^{20}D 1.4761.[7] Deacetylation by heating overnight with an aqueous barium carbonate suspension gave slightly impure *dl*-tetrahydropyrethrolone in 54% yield, b. p. 110–112° (0.3 mm.), n^{28}D 1.4990; but similar hydrolysis of undistilled bromotetrahydropyrethrone gave purer *dl*-tetrahydropyrethrolone in 35% yield, b. p. 118–120° (0.3 mm.), n^{25}D 1.4921, Fehling test on warming, no solid osazone (calcd. for $C_{11}H_{18}O_2$: C, 72.53; H, 9.98. Found: C, 71.1; H, 9.74, average of three analyses); 3,5-dinitrobenzoate, m. p. 105–105.5° (calcd. for $C_{18}H_{20}O_7N_2$: C, 57.44; H, 5.36. Found: C, 57.3; H, 5.05); semicarbazone, m. p. 170.2–170.6° (calcd. for $C_{12}H_{21}O_7N_2$: C, 60.22; H, 8.85. Found: C, 60.4; H, 8.60), absorption maximum at 2635 Å., ϵ = 23,200 in ethanol; methyl ether semicarbazone, m. p. 122.5–123°. The best constants reported are: tetrahydropyrethrolone, b. p. 135–136° (1 mm.),[8] n^{20}D 1.4900–1.4907[8]; *dl*-semicarbazone, m. p. 172–173°,[8] 171–173°,[9] absorption maximum at 2650 Å., ϵ = 22,700[9]; *dl*-methyl ether semicarbazone, m. p. 122–123°.[7]

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(3) Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946); Djerassi and Scholz, *Experientia*, **3**, 107 (1947).

(4) Buu-Hoï, *ibid.*, **2**, 310 (1946).

(5) Meystre and Wettstein, *ibid.*, **2**, 408 (1946).

(6) Clutterbuck and Reuter, *J. Chem. Soc.*, 1467 (1935).

(7) Gillam and West, *ibid.*, 645 (1944).

(8) LaForge and Barthel, *J. Org. Chem.*, **10**, 117 (1945).

(9) West, *J. Chem. Soc.*, 463 (1946).

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RECEIVED MAY 31, 1947

ELECTRON DEFICIENT COMPOUNDS. III. THE BRIDGE STRUCTURE FOR B_2H_6

Sir:

Recently Burg has shown that there are no acidic hydrogens in B_2H_6,[1] and suggests that adoption of the "protonated double bond"[2] structure is inadvisable. Though they make the term "protonated" inappropriate, Burg's experiments do not invalidate the bridge structure. They do help settle the type of bonding in the bridge, if the bridge model is accepted.

It can be shown[3] that a hydrogen atom can be more strongly bound by one electron pair through two boron orbitals than one. The bond energy of a $\overline{\text{B–H–B}}$ bridge may well be of the order of 30% greater than a B–H bond.[3] Hence, the bridge hydrogens should not be acidic.

Pitzer[2] did not state what a "protonated double bond" meant in terms of bond orbitals. One interpretation is that sp^2 orbitals of each boron are used to form two B–H bonds and one B–B bond. The p-orbitals from each boron might then overlap with the s-orbital of hydrogens above and below the plane of the molecule. Then one electron pair would bind two hydrogens, which would carry formal charges ($+{}^1/_2$), would be weakly bound and acidic.

In another interpretation tetrahedral orbitals of boron are used, with each bridge hydrogen at the intersection of orbitals from each boron, and no boron–boron bond.[3] Since the B–H bond energy is greater than the B–B, and since no formal charges are introduced, this structure must

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(1) A. Burg, THIS JOURNAL, **69**, 747 (1947).

(2) K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

(3) R. Rundle, "Electron Deficient Compounds I and II," submitted for publication in THIS JOURNAL. This concept was presented before the Division of Physical and Inorganic Chemistry, The American Chemical Society Convention, April, 1947.