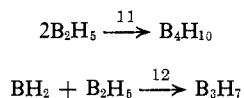In order for (10) to be the predominant terminating step, R_{10} must be larger than the rates of the other possible termination steps which are

$$2B_2H_5 \xrightarrow{11} B_4H_{10}$$

$$BH_2 + B_2H_5 \xrightarrow{12} B_3H_7$$

For the same conditions as above R_{10} will be greater than R_{11} and R_{12} only if these last reactions have small steric factors and nonzero activation energies. This is not unreasonable as the reactions are not simple radical recombinations as is (10). Because the products B_3H_7 and B_4H_{10} have relatively complex structures,[20] considerable rearrangement and orientation is required in the respective activated complexes.

As mentioned above, the experimental facts which are perplexing in terms of the borane mechanism can be explained in the framework of this mechanism. The facts that the pyrolysis involves both BH_2 and BH_3 and that the order changes with temperature have already been discussed. If one of the reactions of B_2H_4 is the rapid condensation to polymer with the elimination of hydrogen, the mechanism accounts for the fact that polymer formation occurs to a significant extent even at relatively low fractions of diborane decomposition.[10] If one allows (5) to be reversible, the inhibition by hydrogen of the reaction[5] and of the formation of polymer[21] follows naturally. To calculate the rate expression, however, would require explicit knowledge of the fate of B_2H_4 and thus is not included here.

An important point in favor of this mechanism is that the explanation of the large normal kinetic isotope effect ($k_H/k_D = 5$) observed in the production of hydrogen from diborane[8] also follows readily. It is quite clear that the main contribution to the isotope effect will be from step 5, a unimolecular decomposition involving the rupture of a boron–hydrogen bond. If approximations suitable for isotopic hydrogen in heavy molecules are made and if it is assumed that all three hydrogen vibrations are lost on passing into the transition state,[22] then taking the B–H stretching frequency $= 2500$ cm.$^{-1}$ and the two bending frequencies together $= 2000$ cm.$^{-1}$, $k_H/k_D = 5$ in excellent agreement with the experiment.

Perhaps as important is the fact that this mechanism suggests a starting point for an explanation of the ambiguous results on the reaction of diborane with ethylene[2,23] and on other systems.[2] One must conclude that on the basis of presently available data, the radical chain mechanism proposed here is an appealing one. One cannot, however, eliminate the borane mechanism as a parallel path although it at least seems clear that the latter mechanism does not predominate.

(20) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.
(21) T. P. Fehlner and W. S. Koski, J. Am. Chem. Soc., 86, 1012 (1964).
(22) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press, New York, N. Y., 1960.
(23) A. T. Whatley and R. N. Pease, J. Am. Chem. Soc., 76, 835 (1954).

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A New L-α-Amino Acid from Lepidoptera

Sir:

Cold methanol extraction of light yellow pigmented areas in the wings and bodies of a large number of Ithomid and Heliconian butterflies[1] has yielded a new L-α-amino acid (0.05–0.7 mg./insect) for which structure I (L-8-hydroxy-1,2,3,4-tetrahydro-4-oxoquinaldic acid = L-dihydroxanthurenic acid) has been established. A representative of a new class of substituted quinoline derivatives,[2] I also presents the interesting possibility (presently under investigation) of forming with xanthurenic acid (IIa) an oxidation–reduction couple in insect metabolic processes.[3]
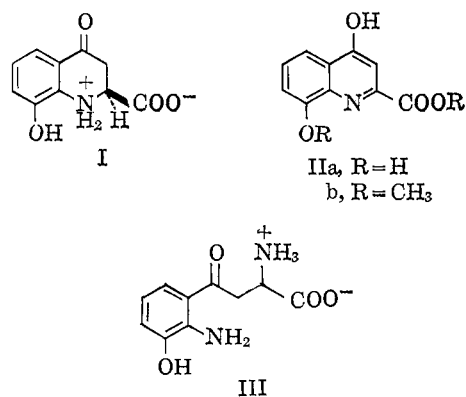
The crystalline pigment, m.p. 185–190° dec., $[\alpha]^{20}$D $-45°$ (c 0.9, MeOH), $+18°$ (c 0.9, MeOH–HCl), ninhydrin positive, showed in the infrared (KBr) bands typical for a zwitterionic α-amino acid (3000–2000, 1610, 1540, and 1400 cm.$^{-1}$) and a highly conjugated carbonyl (vinylogous amide, comparable to γ-pyridone; 1630 cm.$^{-1}$). Acetylation gave a mixture showing absorption for phenol acetate ($\nu_{max}^{CHCl_3}$ 1760 and 1210 cm.$^{-1}$); methylation afforded an oil showing (as film) absorption for saturated methyl ester (1740 and 1175 cm.$^{-1}$), aromatic methoxyl (2870, 1450, 1360, and 1030 cm.$^{-1}$), and γ-pyridone type groupings (3380, 1650, and 1550 cm.$^{-1}$). The n.m.r. spectrum (100 Mc., CD_3COOD)[4] revealed the presence of three adjacent aromatic protons (δ 7.30, doublet; 6.93, doublet; and 6.58, triplet, all J values 8 c.p.s.) and three additional protons as deshielded methylene (δ 3.65) and methine (δ 4.5) groups. The ultraviolet

(1) These are of subfamily Ithomiinae and genus Heliconius of subfamily Heliconiinae, two large neotropical groups of the family Nymphalidae; almost all members of these groups examined stored the amino acid in body and wings. A distantly related nymphalid, the female of Catonephele numilia (a mimic of Heliconius sara), also stored the pigment in the fore wings, and other related species stored a closely related compound of as yet uncertain structure. See also footnote 3. Complete distribution data for the pigment will be presented along with taxonomic comments in a paper to the Journal of the Lepidopterists' Society.
(2) Although dihydrocarbostyril- and dihydroisocarbostyrilcarboxylic acids have been reported, no mention was noted in the literature of any derivative of any 2,3-dihydro-4(1H)-quinolonecarboxylic acid.
(3) The pigment I in an insect is readily detectable by its solubility in cold MeOH, bright yellow fluorescence, R_f on paper chromatography (0.45 in the system BuOH–HOAc–H₂O 4:1:5), and characteristic ultraviolet spectrum (in purer samples; see below). Thus, I appeared to be present in small quantities in the bodies and/or wings of a wide variety of Lepidoptera which did not specifically store it in pigmented areas. Xanthurenic acid also seemed to be present in small quantities in many species and has already been reported in the silkworm, Bombyx mori (K. Inagama, Nippon Sanshigaku Zasshi, 24, 295 (1955)) and Drosophila (Y. Umebachi and K. Tsuchitani, J. Biochem. (Tokyo), 42, 817 (1955)).
(4) The author is grateful to Dr. Lois Durham of Stanford University, Calif., for the n.m.r. measurements. Values are in δ (p.p.m.) from tetramethylsilane as internal reference.

spectra in acidic and neutral solutions showed great similarity to those of 3-hydroxykynurenine (III),[5] while the bathochromic shifts in the three peaks upon passing from neutral to alkaline solution were closely parallel to those observed for m-hydroxyacetophenone[6] (see Table I).

Table I. Ultraviolet Spectra (EtOH)[a]

			3-Hydroxy-kynurenine		m-Hydroxy-acetophenone	
	←——I——→					
1 N HCl	365	(350)	370	(740)		
	320	(1,520)	315	(2,650)		
	254	(4,040)	252	(8,750)		
	218	(6,200)	b		308	(2,300)
					251	(9,100)
Neutral	378	(3,070)	370	(4,250)	215	(17,600)
	273	(5,100)	269	(9,840)		
	235	(13,800)	b			
1 N NaOH	414	(2,660)			349	(2,400)
	292	(5,150)	b		266	(5,000)
	253	(13,600)			234	(22,800)
Δ, neutral	+36				+41	
− alkali	+19				+15	
	+18				+19	

[a] λ_{max}, mμ (ϵ). [b] Not measured.

The high-resolution mass spectrum of I revealed its composition as $C_{10}H_9NO_4$ (M$^+$ at m/e 207.05411; calcd. 207.05315), and showed prominent peaks for loss of CO_2 (m/e 163.06360 = $C_9H_9NO_2$, calcd. 163.06332); COOH (m/e 162); COO(H) + CO (+ H) (m/e 133.05265, 134.06037, and 135.06809 = $C_8H_{7-9}NO$, calcd. 133.05276, 134.06059, and 135.06841; ions a, b, and c); COOH + C_2H_2 (m/e 136.03966 = $C_7H_6NO_2$, calcd. 136.03985; ion d); and CO_2 + CO + CH_8 (m/e 120.04473 = C_7H_6NO, calcd. 120.04494; ion e).[7]

Air oxidation of I in basic solution gave xanthurenic acid (IIa), identical with synthetic material[8] by paper chromatography in two widely differing systems. Furthermore, oxidation of the dimethyl derivative of the pigment (see above) with chloranil in refluxing benzene gave methyl 4-hydroxy-8-methoxyquinaldate (IIb), shown identical with synthetic material[8] by melting point and mixture melting point (undepressed), infrared spectrum (superimposable), thin-layer chromatography, and fluorescence (brilliant yellow-white).

The absolute configuration of the natural pigment was inferred as L through the large positive molecular rota-

(5) C. E. Dalgliesh, Biochem. J., 52, 3 (1953). While I, by infrared, is clearly zwitterionic in the crystalline state, the basic nitrogen appears to remain unprotonated in neutral ethanolic solution.

(6) L. Doub and J. M. Vandenbelt, J. Am. Chem. Soc., 71, 2414 (1949).

(7) The author is especially indebted to Dr. Dieter Becher of Stanford University for the high-resolution mass spectral work on I, which aided materially in the resolution of its structure. Appropriate metastable peaks were observed for most fragmentations. For a discussion of the expulsion of CO from phenols (leading to the alternative structures for a, b, c, and e), see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, pp. 167, 168.

(8) Synthesized by a minor variant of the published method (A. Furst and C. J. Olsen, J. Org. Chem., 16, 412 (1951)), in which the initial condensation was effected at 0° spontaneously and in quantitative yield with o-anisidine and dimethyl acetylenedicarboxylate (K. S. Brown, Jr., unpublished investigations). The author thanks Professor F. Feigl and Dr. A. Roseira for generous donations of o-anisidine, and Dow Quimica do Brasil S. A. for a sample of Dowtherm A.

a(m/e133)   b(m/e134)   c(m/e135)   d(m/e136)

e(m/e120)
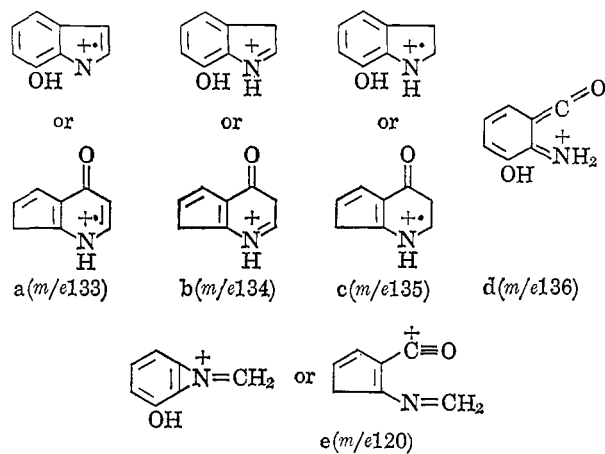
tion change (+130° in MeOH) observed upon passing from the neutral to the protonated form.[9]

Besides being a new butterfly pigment, compound I probably represents a new metabolite of tryptophan. Further work is presently under way to study its biogenesis[10] and to investigate its possibly wider role in insect metabolism.[3,10]

(9) This property, characteristic in aqueous solutions for α-amino acids possessing the L-configuration, should not be expected to change qualitatively in methanolic solution. See J. S. Fruton and S. Simmonds, "General Biochemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 97.

(10) Compound I could theoretically be produced either by stereospecific cyclization of β(o-amino-m-hydroxybenzoyl)acrylate (see A. Butenandt, U. Scheidt, and E. Biekert, Ann., 586, 229 (1954), in which I is suggested as a nonisolable intermediate in the base-catalyzed in vitro cyclization of 3-hydroxykynurenine to xanthurenic acid) or by stereospecific reduction of xanthurenic acid in the insect (see footnote 3). The presently accepted pathway for the biosynthesis of xanthurenic acid (spontaneous cyclization of the α-ketocarboxylate resulting from transamination of 3-hydroxykynurenine) would probably favor the latter pathway.

(11) The author gratefully acknowledges financial assistance from the Rockefeller Foundation in support of a joint research project between Stanford University and the Universidade do Brasil, on Brazilian natural products. Some initial experiments leading to this work were performed by Dr. Ed Paschoal Carrazzoni of the Universidade do Recife. Special thanks are due to Dr. Olaf Mielke of the Museu Nacional, Rio de Janeiro, for his assistance in location, collection, and identification of the insects studied. The author is indebted to Prof. Carl Djerassi of Stanford University for his inspiration, guidance, and assistance during the course of this work.

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Additions of Iodine Azide to Olefins.
Stereospecific Introduction of Azide Functions[1]

Sir:

The chemistry of organic and inorganic azides attracted renewed attention recently when it was shown that these compounds are useful in the generation of nitrene intermediates and in the synthesis of a variety of heterocyclic compounds.[2] In connection

(1) (a) Stereochemistry of Organic Nitrogen Compounds. VI. For paper V see A. Hassner and W. A. Wentworth, Chem. Commun. (London), 44 (1965). (b) Support of this work by Grant 2004A1,4 from the Petroleum Research Fund, American Chemical Society, and by Grant CA4474 of the National Institutes of Health is gratefully acknowledged.

(2) See, for instance (a) D. H. R. Barton and A. N. Starratt, J. Chem. Soc., 2444 (1965); (b) F. D. Marsh and M. E. Hermes, J. Am. Chem. Soc., 86, 4506 (1964); (c) R. Huisgen, Angew. Chem. Intern. Ed. Engl., 2, 565 (1963); (d) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, Chem. Ind. (London), 1556 (1964); (e) W. Lwowski and T. W. Mattingly, Jr., J. Am. Chem. Soc., 87, 1947 (1965).