was distilled carefully through a semi-micro column. The yield of the debromination product (II) was 0.98 g. (77%), b.p. 107° (746 mm.), $n^{25}D$ 1.4058.

The reaction of bromine (3 g.) with II (2.0 g.) in 10 ml. of carbon tetrachloride at −10° proceeded rapidly and afforded 4.85 g. (93.5%) of the dibromoester (IV), b.p. 70.5° (0.8 mm.), $n^{25}D$ 1.5112, which was identical with the product obtained by the action of N-bromosuccinimide on II.

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2,2,4-Trimethyl-1,2-dihydroquinoline

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Recently Johnson and Buell[1] prepared 1,2-dihydroquinoline. On the basis that its ultraviolet absorption spectrum, which had three peaks, was strikingly similar to that of the so-called "acetone anil," they opined that a 1,4-dihydro structure for the latter compound is eliminated. Incidentally, they also stated that 1,4-dihydroquinoline, unlike the 1,2-dihydroquinoline, should have a spectrum similar to that of 1,2,3,4-tetrahydroquinoline. On the contrary, the 1,4-dihydro derivative as a vinylamine has a double bond conjugated with the nitrogen atom[2] and hence its spectrum would not be like that of the 1,2,3,4-tetrahydroquinoline. Nevertheless, their assignment of structure is correct for the dihydroquinolines, in our opinion, not for other reasons given by them but for reasons set forth in the present note.

The spectrum of the trimethyldihydroquinoline[3] (0.00625 g./l.) in methanol, 1,2 *N* in HCl, is shown in Fig. 1. The doublet at 259 and 255 mμ and *E* 53 (log ε 13.96) can be compared to the single band observed for α-methylstyrene at 242 mμ and log ε 4.03 or better still, since the open-chain methyl group here inhibits resonance, to the peak for the cyclic analog 1-methyl-3,4-dihydronaphthalene which Ramart-Lucas and Hoch[4] found to be at 259 mμ, log ε 3.8. Morton and de Gouveia[5] found 1,2-dihydronaphthalene to have a maximum at 262 mμ, log ε 4.0, and 1,4-dihydronaphthalene was found to have a doublet at 267 and 274 mμ, log ε 2.9. It is thus apparent that the spectrum of the trimethyldihydroquinoline in acid solution (the acid is present in order to remove any ability of the nitrogen atom to conjugate with the benzene ring or double bond) requires that a double bond must be conjugated with the benzene ring, thus finally proving the structure of 2,2,4-trimethyl-1,2-dihydroquinoline.

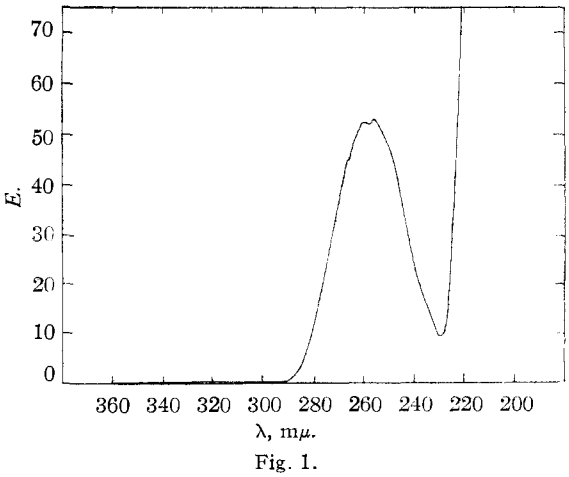

Fig. 1.

Since first submitting the present note, Dr. Paul Downey pointed out to us that Bohlmann[6] has recently reported 1,2-dihydroquinoline, m.p. 40–41° to result from the reaction of $LiAlH_4$ with quinoline. In our hands Bohlmann's directions gave a 90% yield of product which, if purified by extraction with cyclohexane, melted at 72–74°, and which had nearly the same absorption spectrum and other properties reported by Johnson and Buell for their dihydroquinoline. It was unstable in air and in acid solutions so that the absorption spectra in such solutions apparently could not be applied to the elucidation of the structure of the dihydroquinolines. Dr. Franz Widmer found in our laboratory that this compound, like N-phenyl-3,5-diethyl-2-propyl-1,4-dihydroquinoline,[2] evolves hydrogen (about one-third mole) when first contacted with reduced PtO_2 in acetic acid. Subsequently, hydrogen (a net amount of four moles) is absorbed by the acetic acid solution. This confirms Johnson and Buell's finding that their dihydroquinoline, which obviously is the same as Bohlmann's, readily undergoes dehydrogenation.

(1) W. S. Johnson and B. G. Buell, THIS JOURNAL, **74**, 4518 (1952).

(2) Compare the spectrum of an N-phenyl-1,2-dihydropyridine, D. Craig, L. Schaefgen and W. P. Tyler, *ibid.*, **70**, 1626 (1952); see also the spectra for eneamines quoted by Johnson and Buell.

(3) D. Craig, *ibid.*, **60**, 1458 (1938).

(4) P. Ramart-Lucas and N. J. Hoch, *Bull. soc. chim.*, [5] **5**, 848 1938).

(5) R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 916 (1934).

(6) F. Bohlmann, *Ber.*, **85**, 390 (1952).

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On the Origin of the Carboxyl Group of Histidine in Yeast[1,2]

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Recently Ehrensvärd, *et al.*,[3,4] have shown by isotopic studies in *Torulopsis utilis*, and Cutinelli, *et al.*,[5] by similar studies in *Escherichia coli*, that when $C^{13}H_3C^{14}OOH$ is administered as a substrate, the carboxyl group of histidine arises exclusively from the methyl carbon atom. This is in contrast to the high C^{14} (acetate carboxyl) incorporation into the carboxyl groups of the other amino acids.

(1) This research was supported by contract number AT (45-1)-301 from the Atomic Energy Commission. Published with the approval of the Monographs Publications Committee, Research paper number 220, School of Science, Department of Chemistry. Presented before the Northwest Regional Meeting of the American Chemical Society, Corvallis, June, 1952.

(2) Taken from a thesis presented by J. W. D. for the M.S. degree, Oregon State College, 1952.

(3) G. Ehrensvärd, L. Reio and E. Saluste, *Acta Chem. Scand.*, **3**, 645 (1949).

(4) G. Ehrensvärd, L. Reio, E. Saluste and R. Stjernholm, *J. Biol. Chem.*, **189**, 93 (1951).

(5) C. Cutinelli, G. Ehrensvärd, L. Reio, E. Saluste and R. Stjernholm, *Acta Chem. Scand.*, **5**, 353 (1951).

TABLE I

RADIOACTIVITIES OF HISTIDINE AND ASPARTIC ACID FRACTIONS FROM YEAST

	Histidine							Aspartic acid[a]			
	Content in yeast, %			Radioactivity,[a] counts/min. × 10^3			Ratio[b] Py/N_2	Radioactivity,[a] counts/min. × 10^3			Ratio[b] Py/N_2
	Py/O_2	Py/N_2	Ac/O_2	Py/O_2	Py/N_2	Ac/O_2	Py/O_2	Py/O_2	Py/N_2	Ac/O_2	Py/O_2
Whole molecule	1.2	1.3	1.1	8.7	6.1	1.8	0.70	25.4	20.6	15.0	0.81
Carboxyl (histidine)				0.48	0.66	0	1.38				
C_3 (aspartic acid)								1.80	2.15	0	1.19

[a] Expressed as counts/minute/mmole amino acid/mmole substrate utilized. [b] Obtained by dividing the specific activity of the whole molecule or particular atom derived from pyruvate anaerobically (under nitrogen) by the corresponding aerobically derived value.

In this Laboratory, radioactive histidine samples were isolated from bakers' yeast (*Saccharomyces cerevisiae*) grown on $CH_3C^{14}OOH$ aerobically and $CH_3C^{14}OCOOH$ both aerobically and anaerobically.[6] The isolations were carried out through ion-exchange resin column operations according to the method of Winters and Kunin.[7] The histidine samples were purified as a new derivative, the monoöxalate, which is readily recrystallized from aqueous ethanol and gives a definite decomposition point.

In the present work, preliminary degradation of the histidine samples has confirmed Ehrensvärd's observation using acetate; however a significant amount of C^{14} has been observed in the carboxyl group in histidine derived from pyruvate.

The specific radioactivities of histidine derived from each of the three experiments and the activities of the respective carboxyl groups are given in Table I.

From acetate, the histidine carboxyl is seen to be completely inactive, as shown previously.[3] The non-incorporation of acetate carboxyl into histidine carboxyl thus rules out the possibility of union of an imidazole ring with a C_3-unit (such as pyruvate) which might be produced through condensation of a C_2-compound with (radioactive) metabolic CO_2.

Among other possible intermediates in histidine biosynthesis, the C_4-acids deserve consideration. The pattern of labeling in oxalacetate, for example, may be presumed to be similar to the corresponding pattern in aspartic acid in this yeast.[8] In turn, the radioactivity of the methylene carbon (C_3) of aspartic acid furnished an index of histidine carboxyl (C_1) activity. Thus, from pyruvate, incorporation of C^{14} into both these atoms was similarly higher in the *anaerobic* sample (anaerobic/aerobic ratio = 1.38 in aspartate C_3, and 1.19 in histidine C_1) in spite of the fact that these amino acids as a whole showed greater specific radioactivity after *aerobic* growth. Finally, from acetate, both C_3 of aspartate and C_1 of histidine were unlabeled.

Experimental

Isolation of Histidine.—Histidine was isolated from hydrolyzed yeast protein previously freed from arginine, glutamic acid, aspartic acid, tyrosine and lysine.[9] The histidine, after a fivefold dilution with non-radioactive histidine, was adsorbed on an IRC-50 ion-exchange resin column (Rohm and Haas), buffered at *p*H 4.7 with sodium acetate, from which it was eluted with 4% hydrochloric acid solution. The eluate was repeatedly evaporated to dryness by distillation under reduced pressure to remove free hydrochloric acid and dissolved in water. An excess of silver nitrate was then added. The silver chloride was removed by centrifugation and the *p*H of the centrifugate adjusted to *p*H 7.4 to precipitate the silver salt of histidine. The washed silver salt was suspended in water and decomposed with hydrogen sulfide. Removal of the silver sulfide and evaporation of the filtrate under reduced pressure yielded crude histidine which was purified as the monoöxalate.

Purification of Histidine.—The histidine from the foregoing procedure (80–100 mg.) was dissolved in 2 to 4 ml. of water and mixed with a 100% excess of oxalic acid as a saturated solution. Alcohol was added to a concentration of approximately 80%. The white solid that formed was allowed to stand for 12 hours at 0°, then filtered and recrystallized by dissolving in water and reprecipitating with alcohol. The recrystallized material had a decomposition point beginning sharply at 223° (Fischer block, corrected). Over-all yields of 50 to 80% were experienced in this operation on a 100-mg. scale.

Anal. Calcd. for histidine monoöxalate: C, 39.2; H, 4.5; equiv. wt. of oxalate, 122.60; histidine, 63.4. Found: C, 39.9; H, 4.8; equiv. wt. of oxalate ($KMnO_4$), 122.5; histidine (microbiological assay), 67.

Radioactivity Measurements.—The specific radioactivities of histidine oxalate samples were determined by direct plating, using appropriate counting times for samples and backgrounds to maintain an over-all precision of 5%.[10] The carboxyl group specific radioactivities were determined by ninhydrin decarboxylation[11] after preliminary "cold" runs had established that satisfactory yields of barium carbonate could be obtained[4] and that oxalic acid gave no CO_2 with ninhydrin. The $BaC^{14}O_3$ thus obtained was plated and counted in the conventional manner with the usual correction for self-absorption applied.

(6) C. H. Wang, R. F. Labbe, B. E. Christensen and V. H. Cheldelin, *J. Biol. Chem.*, **197**, 645 (1952).

(7) J. C. Winters and R. Kunin, *Ind. Eng. Chem.*, **41**, 460 (1949).

(8) C. H. Wang, R. C. Thomas, V. H. Cheldelin and B. E. Christensen, *J. Biol. Chem.*, **197**, 663 (1952).

(9) R. F. Labbe, R. C. Thomas, V. H. Cheldelin, B. E. Christensen and C. H. Wang, *ibid.*, **197**, 655 (1952).

(10) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 288.

(11) *Ibid.*, pp. 260–261.

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Freezing Point and Vapor Pressure Data for Solutions of Carbon Dioxide with Some Halogen Substituted Methanes

BY THOMAS DE VRIES AND WILLIAM N. VANDERKOOI

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Vapor pressure–composition data were desired for liquid mixtures of carbon dioxide with bromochloromethane, dibromodifluoromethane and bromotrifluoromethane. The solutions were prepared by condensing successive measured volumes of carbon dioxide gas into the liquid organic compound which was in a bulb attached to a closed system and cooled by immersion in a *n*-propyl