H, 6.65; O, 22.87; N, 6.16; S, 3.52. Found: C, 60.90, 61.23; H, 6.52, 6.52; O, 22.86; N, 6.07, 6.15; S, 3.43. Analytical data for leurosine and vincaleukoblastine are in agreement with a tentative formulation as isomeric $C_{46}H_{58}O_9N_4$ compounds.[6] Their ultraviolet spectra are superimposable: λ_{max}^{EtOH} 214 mμ (log a_M 4.74), 259 mμ (log a_M 4.22), and λ_{min}^{EtOH} 246 mμ (log a_M 4.14); shoulders at 288 mμ (log a_M 4.15) and 296 mμ (log a_M 4.12).

The close structural relationship of these two alkaloids is demonstrated further by their essentially identical infrared spectra. The major differences occur in the hydroxyl region of vincaleukoblastine with additional bands at 2.80 and 9.91 μ.[7]

(6) An alternate C_{18} formulation was discarded on the basis of electrometric titrations, carbon–oxygen ratios and functional group analyses as presented in the following communication.

(7) For these spectra, see communication IV, p. 4745.

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THE DIRECT FLUORINATION OF UREA: THE SYNTHESIS AND PROPERTIES OF DIFLUORAMINE

Sir:

The direct fluorination of urea at 0° yields a complex yellow, corrosive liquid which contains up to 16% active fluorine (to HI) and about 45–55% total fluorine. On solution in water, ammonium fluoride, biurea and unidentified refractory solids are obtained.[1] Distillation of the liquid from Kel-F or polyethylene into glass yields, in the more volatile fraction, CO_2, SiF_4, HNCO, COF_2 and difluoramine, HNF_2.[2] As high as 15% of the original fluorine has been recovered as difluoramine.

Ruff and Staub[3] first reported the preparation of difluoramine but gave no analysis and erroneous physical properties. They also reported that it did not react with aqueous hydriodic acid, which we observed. Therefore, we agree with Kennedy and Colburn[2] that the material described by Ruff and Staub was not difluoramine. Our vapor pressure data agree with Kennedy and Colburn's within experimental error and the infrared spectra are identical. However, our mass spectrum and melting point do differ.

We found that gaseous difluoramine loses hydrogen on contact with various solids to form the recently reported tetrafluorohydrazine.[4] With lithium hydride as a catalyst, yields of 70% are obtained easily. When chilled to −196°, solid difluoramine tends to detonate spontaneously. Chilling only to −142° and working with small samples, minimizes this tendency, but the violence of the reaction requires adequate precautions be taken. Physical properties we determined are listed in Table I.

(1) O. Glemser and H. Ludemann, *Z. anorg. allgem. Chem.*, **286**, 168 (1956).

(2) A. Kennedy and C. Colburn, THIS JOURNAL, **81**, 2906 (1959).

(3) O. Ruff and L. Staub, *Z. anorg. allgem. Chem.*, **198**, 32 (1931).

(4) C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).

TABLE I

THE PHYSICAL PROPERTIES OF DIFLUORAMINE

Melting point, °C.	−116 ± 3°
Boiling point, °C.	−23.6°
Density	$d = 1.424 - 0.00202t$
Trouton constant	23.7

Difluoramine was identified by its molecular weight (calculated for HNF_2, 53.02; observed, 54) and its almost instantaneous and quantitative reaction with 0.75 *N* HI according to the equation

$$HNF_2 + 4HI \longrightarrow 2I_2 + NH_4F + HF$$

The mass spectrum taken with a CEC Model 103C mass spectrometer (Table II) is consistent with the above formulation. All of these peaks are reproducible on different samples.

TABLE II

MASS SPECTRUM OF DIFLUORAMINE

m/e	Pattern coef.	+ Ion
14	19.37	N
15	10.50	HN
19	6.89	F
20	1.95	HF
28	1.61	N_2
33	34.35	NF
34	100.00	HNF
52	1.5	NF_2
53	66.97	HNF_2

Sensitivity *n*-butane *m/e* 43 = 69.89 div./μ.
Sensitivity HNF_2 *m/e* 34 = 23.12 div./μ.
Ionizing voltage 70 v.
Ionizing current 10 μa.

The authors are indebted to the Office of Naval Research for support of this work. The mass spectral determination was performed by Mr. Mario Stevens of this laboratory. Mr. Martin Epstein participated in the initial work.

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UNSATURATED MACROCYCLIC COMPOUNDS. XI.[1] CYCLOTETRACOSA-1,3,7,9,13,15,19,21-OCTAENE-5,11,17,23-TETRAYNE AND CYCLOTETRACOSA-1,3,5,7,9,11,13,15,17,19,21,23-DODECAENE

Sir:

We wish to report the synthesis of the completely conjugated 24-membered ring cyclic systems named in the title.

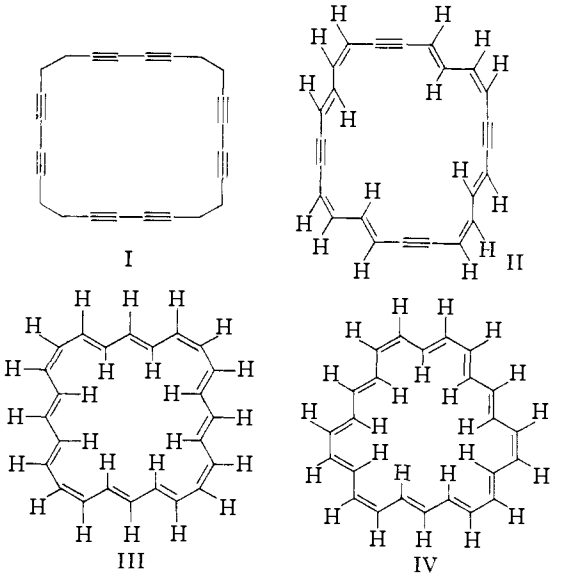
Cyclotetracosa-1,3,7,9,13,15,19,21-octayne (I) (the cyclic "tetramer" of 1,5-hexadiyne)[2] on treatment with potassium *t*-butoxide in *t*-butanol–benzene at 90° for 30 minutes underwent a similar rearrangement to that of the corresponding "trimer."[3] The product, formed in *ca.* 40% yield, was obtained as dark purple prisms from ether (red in solution), which decomposed when heated.

(1) Part X, F. Sondheimer and Y. Gaoni, THIS JOURNAL, in press.

(2) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 4247 (1957).

(3) F. Sondheimer and R. Wolovsky, *ibid.*, **81**, 1771 (1959).

The empirical formula was $C_{24}H_{16}$ (Found: C, 94.65; H, 5.20): $\lambda_{max.}^{chloroform}$ 240, 330 and 346 mμ (ϵ = 28,000, 125,000 and 206,000); $\lambda_{max.}^{benzene}$ 333 and 350 mμ (ϵ = 120,000 and 208,000), with absorption up to *ca.* 600 mμ ($\epsilon_{400\ m\mu}$ = 2,270, $\epsilon_{450\ m\mu}$ = 2,020, $\epsilon_{500\ m\mu}$ = 1,070, $\epsilon_{550\ m\mu}$ = 275). The infrared spectrum (KBr) showed bands at 3.31(m), 4.63 (w), 6.28(m), 7.07(m), 7.72(m), 8.49(m), 9.11(m), 10.27(s), 10.75(s), 11.81(m), 13.11(m) and 13.24 (m). Hydrogenation in dioxane over platinum smoothly yielded cyclotetracosane, m.p. and mixed m.p. 46–47°.



I II III IV

This rearrangement product is clearly a completely conjugated octaene-tetrayne. It is most likely cyclotetracosa-1,7,13,19-tetra-(*cis*)-ene-3,9,-15,21-tetra-(*trans*)-ene-5,11,17,23-tetrayne (II), a molecule which may be not completely planar in view of the presence of four *cis*-double bonds.

Partial hydrogenation of II in benzene over a "Lindlar" palladium catalyst[4] followed by chromatography on alumina gave first a yellow crystalline compound ($\lambda_{max.}^{pentane}$ 306 and 314 mμ), then unchanged II and finally *ca.* 15% of a substance crystallizing from ether as very dark-blue, almost black, needles (dark violet in solution). The last compound, which decomposed when heated, had empirical formula $C_{24}H_{24}$ (Found: C, 92.14; H, 7.62); $\lambda_{max.}^{isooctane}$ 264, 350, 363 and 512 mμ (ϵ = 12,100, 195,000, 201,000 and 1,740); $\lambda_{max.}^{benzene}$ 360, 375 and 530 mμ (ϵ = 183,000, 195,000 and 1,720), with absorption up to *ca.* 750 mμ ($\epsilon_{600\ m\mu}$ = 1,270, $\epsilon_{650\ m\mu}$ = 610, $\epsilon_{700\ m\mu}$ = 180). The infrared spectrum (KBr) showed bands at 3.32 (m), 7.06(w), 7.73(m), 10.13(s), 10.36(s), 10.55(s), 10.77(w), 10.90(w), 11.47(w), 12.03(w), 12.25(w), 12.85(w) and 13.28(m). Full hydrogenation gave cyclotetracosane, m.p. and mixed m.p. 44–46°.

The properties of the blue substance show it to be cyclotetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaene (CTD). The ultraviolet spectrum and color indicate that all 12 double bonds are part of one chromophoric system and *trans*-addition of hydrogen therefore appears to have taken place, as in the synthesis of cycloöctadecanonaene (CON).[5] The present evidence does not permit a definite distinction to be made between the 1,7,13,19-tetra-(*cis*)-ene structure III and the 1,9,17-tri-(*cis*)-ene structure IV. We consider, however, that the spectral evidence favors IV (requiring the inversion of one *cis*-double bond of II during the hydrogenation), the more planar structure of the two. It should be noted that CTD cannot be converted to a more stable isomer, *e.g.*, with iodine in boiling benzene.

CTD is a 24π-electron system and, unlike CON,[5] does not comply with Hückel's rule for aromaticity [presence of $(4n + 2)$ π-electrons]. In fact, CTD is much less stable than CON. Thus, CTD in daylight and air at room temperature after 24 hr. is over 99% destroyed, while CON is unchanged; CTD in dilute benzene solution in daylight after 12 days is 80% destroyed, while CON is largely unchanged.

(4) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(5) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. 3, 3 (1959).

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METABOLISM OF DL-PIPECOLIC ACID-2-C^{14} [1]

Sir:

Pipecolic acid (piperidine-1-carboxylic acid) was found to be a product of lysine catabolism in the rat,[2] in plants[3] and in *Neurospora*.[4] The suggestion that this compound was an intermediate between lysine and α-aminoadipic acid[2] was based only on the scanty evidence of a small conversion of lysine to α-aminoadipic acid observed in guinea pig liver homogenate,[5] and the fact that both lysine and α-aminoadipic acid form glutaric acid.[2,5] The present communication presents data which show that pipecolic acid does indeed lie on the lysine pathway to α-aminoadipic acid and confirms the role of the latter compound in lysine breakdown in the rat.

DL-Pipecolic acid-2-C^{14} (specific activity 0.3 mc./mmole) was prepared by enzymic deamination of DL-lysine-2-C^{14} and hydrogenation of the product.[6] The material was shown to be pure by paper chromatography and autoradiography.

Labeled pipecolic acid (1μc.) was incubated at 37° for 1.5 hours in each of three flasks containing: 2 ml. of rat liver mitochondria prepared in 0.25 *M* sucrose; 50 μmoles of phosphate buffer, *p*H 7.4; 3 μmoles of ATP; 3 μmoles of Versene; 12 μmoles of Mg^{++}; 25 μmoles of L-α-aminoadipate; the total volume was 3 ml./flask.

After deproteinization, the combined media were fractionally eluted from Dowex 50-(H^+) with 1 *N* HCl. The L-α-aminoadipic acid was located with ninhydrin.

(1) Aided by research grant (T-89A) from the American Cancer Society and the cancer research funds of the University.

(2) M. Rothstein and L. L. Miller, *J. Biol. Chem.*, **211**, 851 (1954).

(3) N. Grobbelaar and F. C. Steward, THIS JOURNAL, **76**, 4341 (1953).

(4) R. S. Schweet, J. T. Holden and P. H. Lowy, *J. Biol. Chem.*, **211**, 517 (1954).

(5) H. Borsook, C. L. Deasy, A. J. Haagen-Smit, G. Keighley and P. H. Lowy, *ibid.*, **176**, 1383 (1948).

(6) A. Meister, *ibid.*, **206**, 577 (1954).