1014. *Carcinogenic Nitrogen Compounds. Part XLVII.*[1] *γ-Carbolines and 2,10-Diaza-anthracenes Isosteric with Benzocarbazoles and Benzacridines*

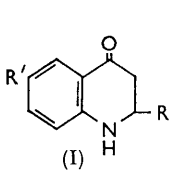
By Odette Roussel, N. P. Buu-Hoï, and P. Jacquignon

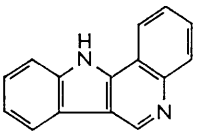
The synthesis has been investigated of a number of benzo-, dibenzo-, and pyrido-derivatives of γ-carboline and 2,10-diaza-anthracene which are structurally related to the carcinogenic angular benzocarbazoles, dibenzocarbazoles, and benz[*c*]acridines.

Recently, it was shown that many pyridine analogues of the three bisangular dibenzocarbazoles are carcinogenic,[2] the importance of this biological effect varying with the position of the pyridine nitrogen atom in relation to the imino-group.[3] This suggested an investigation of the synthesis of further compounds of this type, especially tetra- and penta-cyclic derivatives of γ-carboline.

[1] Part XLVI, D. C. Thang, N. P. Buu-Hoï, and N. D. Xuong, *J.*, 1965, 4585.
[2] A. Lacassagne, N. P. Buu-Hoï, F. Zajdela, P. Jacquignon, and F. Périn, *Nature*, 1961, **191**, 1005.
[3] A. Lacassagne, N. P. Buu-Hoï, F. Zajdela, F. Périn, and P. Jacquignon, *Compt. rend.*, 1963, **257**, 818.

The simplest route was *via* 1,2,3,4-tetrahydro-4-oxoquinoline and its substitution products (I). The unsubstituted ketone was best prepared by direct cyclisation of β-*N*-phenylalanine with polyphosphoric acid; starting from aniline and methyl acrylate, this three-step synthesis gave substantially the same yield as the more elaborate procedures of Clemo and Perkin [4] and of Johnson *et al.*,[5] which involve passing through the *N*-toluene-*p*-sulphonyl derivative of β-*N*-phenylalanine. Even using these latter methods, the preparation of 11*H*-benzo[*a*]-γ-carboline (II) could be simplified by the direct indolisation of 1,2,3,4-tetrahydro-4-oxo-1-toluene-*p*-sulphonylquinoline phenylhydrazone by means of sulphuric acid in acetic acid medium, the cyclisation being accompanied by both detosyl-


(I)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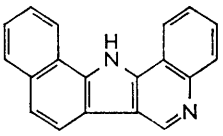
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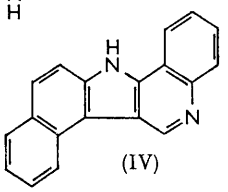
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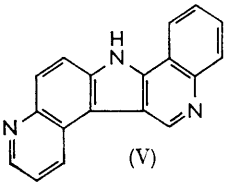
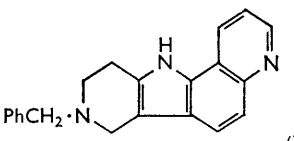

(V)

ation and dehydrogenation. This technique also proved successful for preparing the 8-methyl, and 8,9- and 9,10-dimethyl homologues of (II), as well as 13*H*-dibenzo[*a*,*i*]-γ-carboline (III), which is an isostere of 13*H*-dibenzo[*a*,*i*]carbazole, and 13*H*-dibenzo[*a*,*g*]-γ-carboline (IV) and 7*H*-benzo[*a*]pyrido[3,2-*g*]-γ-carboline (V), isosteres of 7*H*-dibenzo[*a*,*g*]-carbazole. The fact that the dehydrogenation which occurred in the course of all these indolisations was complete, was established by mass spectrometry. 2-Methoxy-derivatives of the heterocycles (II), (III), and (IV) were prepared *via* 1,2,3,4-tetrahydro-6-methoxy-4-oxoquinoline, which was readily obtained by Koo's method.[6] As methyl substitution in the mesophenanthrenic zone is generally favourable for carcinogenic activity[7] the synthesis of 6-methyl homologues of (II), (III) and (IV) was investigated. The obvious intermediate, *viz.*, 1,2,3,4-tetrahydro-2-methyl-4-oxoquinoline, being not readily accessible, a more devious approach was adopted which made use of its readily available 6-chloro-derivative, from which the various γ-carbolines obtained were successfully dechlorinated by means of Raney nickel [8] to give the desired compounds.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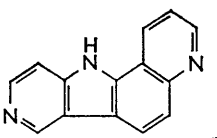
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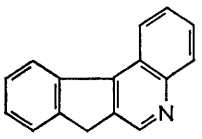
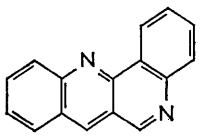
A convenient route to 11*H*-pyrido[2,3-*i*]-γ-carboline (VII) was to use *N*-benzyl-4-piperidone, whose 5-quinolylhydrazone was converted into the tetrahydro-compound (VI), which underwent simultaneous debenzylation and dehydrogenation on heating over palladised charcoal.[9] An attempt to prepare the isostere (VIII) of benzo[*c*]fluorene by applying

[4] G. R. Clemo and W. H. Perkin, jun., *J.*, 1924, **125**, 1609.
[5] W. S. Johnson, E. L. Woroch, and B. G. Buell, *J. Amer. Chem. Soc.*, 1949, **71**, 1901.
[6] J. Koo, *J. Org. Chem.*, 1963, **28**, 1134.
[7] G. M. Badger, J. W. Cook, C. L. Hewett, E. L. Kennaway, N. M. Kennaway, R. H. Martin, and A. M. Robertson, *Proc. Roy. Soc.*, 1940, *B*, 439; M. J. Shear and J. Leiter, *J. Nat. Cancer Inst.*, 1941, **2**, 241.
[8] N. P. Buu-Hoï, N. D. Xuong, and N. V. Bac, *Bull. Soc. Chim. France*, 1963, 2442; *Compt. rend.*, 1963, **257**, 3182.
[9] N. P. Buu-Hoï, O. Roussel, and P. Jacquignon, *J.*, 1964, 708.

to 3-benzylidene-1,2,3,4-tetrahydro-4-oxoquinoline the cyclodehydration method for the synthesis of benzofluorenes,[10] was a failure, the starting material being recovered unchanged even after prolonged heating with polyphosphoric acid. On the other hand, a number of benzo-derivatives of 2,10-diaza-anthracene, which are isosteric with the benz[*c*]acridines, were readily prepared by applying the Pfitzinger reaction to the various 1,2,3,4-tetrahydro-4-oxoquinolines; in most cases, thermal decarboxylation of the highly coloured cinchoninic acids thus obtained was accompanied by spontaneous dehydrogenation, yielding derivatives of dibenzo[*b*,*h*][1,6]naphthyridine (IX) directly, but in some instances the 5,6-dihydro-compound was formed, which was then dehydrogenated over palladised charcoal. The



(VIII)



(IX)

6-methyl homologue of (IX), required for assessing the effect of mesophenanthrenic substitution, was obtained from its 2-chloro-derivative by dehalogenation with Raney nickel, a method that is both more general and more satisfactory than that used by Backeberg.[11] Whereas the derivatives of γ-carboline gave, in some cases, dipicrates, all the dibenzonaphthyridines furnished monopicrates, despite the presence of two quinoline moieties. The structural analogy of the dibenzo[*b*,*h*][1,6]naphthyridines with the corresponding benz[*c*]acridines was reflected in the similarity of their ultraviolet absorption spectra, as had already been observed with other types of heterocycles.[12] Table 1 lists the derivatives of 11*H*-benzo[*a*]-γ-carboline and Table 2 lists the dibenzonaphthyridines and their derivatives. In mass spectrometry, both series of compounds were characterised by their resistance to fragmentation, the highest peaks by far being those of the molecular ions.

Results of biological testing will be reported elsewhere.

Experimental

Preparation of Ketones (I).—Melting points were taken on a Maquenne block. A well-stirred mixture of β-*N*-phenylalanine (7 g.; prepared from aniline and methyl acrylate [5]) and polyphosphoric acid (100 g.; prepared from 3 parts phosphorous pentoxide to 2 parts phosphoric acid) was heated gradually to 130° during 20 min., and kept at that temperature for a further 10 min.; after cooling, the mixture was poured into iced water (300 c.c.), and the precipitate of 1,2,3,4-tetrahydro-4-oxoquinoline obtained after a few hours was washed thoroughly with water, and purified by distillation *in vacuo* (b. p. 195°/20 mm.) and recrystallisation from cyclohexane. The yield, based on the aniline, was 68%; m. p. 45°. 6-Chloro-1,2,3,4-tetrahydro-2-methyl-4-oxoquinoline (I; R = Me, R′ = Cl), m. p. 134°, prepared by Koo's method [6] from β-(*p*-chloroanilino)butyric acid,[13] in 60% yield (based on *p*-chloroaniline), was characterised as its *oxime*, which formed colourless needles, m. p. 150°, from aqueous ethanol (Found: C, 57·0; H, 5·4; N, 13·3. $C_{10}H_{11}ClN_2O$ requires C, 57·1; H, 5·3; N, 13·3%). 1,2,3,4-Tetrahydro-6-methoxy-4-oxoquinoline (I; R = H, R′ = MeO), m. p. 114° (lit.,[14] 112—113°), was similarly prepared, in 55% yield (based on *p*-anisidine).

11H-*Benzo*[a]-*γ-carboline* (II).—A solution of the *N*-toluene-*p*-sulphonyl derivative of 1,2,3,4-tetrahydro-4-oxoquinoline (3·1 g.) and phenylhydrazine (1·1 g.) in ethanol (8 c.c.) was heated with 2 drops of acetic acid for 90 min. at 80°; after cooling and basification with aqueous ammonia, the precipitated 1,2,3,4-*tetrahydro*-4-*oxo*-1-*toluene*-p-*sulphonylquinoline phenylhydrazone* crystallised as colourless needles (3 g.), m. p. 235°, from toluene (Found:

[10] W. S. Rapson and R. G. Shuttleworth, *J.*, 1940, 636; N. P. Buu-Hoï and P. Cagniant, *Rev. sci.*, 1942, **80**, 319, 384, 436.
[11] O. G. Backeberg, *J.*, 1933, 618.
[12] Cf. G. M. Badger in " Six-Membered Heterocyclic Nitrogen Compounds with Three Condensed Rings," ed. C. F. H. Allen, Interscience, New York, 1958, p. 551.
[13] R. C. Elderfield, *J. Amer. Chem. Soc.*, 1946, **68**, 1259.
[14] G. R. Clemo and W. H. Perkin, jun., *J.*, 1925, 2297.

C, 67·8; H, 5·3. $C_{22}H_{21}N_3O_2S$ requires C, 67·5; H, 5·4%). Its indolisation did not require Nordhausen acid,[4] and was effected in 50% yield by heating for 10 min. on a water-bath the solution of the phenylhydrazone (1·5 g.) in acetic acid (10 c.c.) mixed with sulphuric acid (4 c.c.); after cooling and basification with aqueous ammonia, *compound* (II) was recrystallised from methanol, giving microneedles, m. p. 333° (m. p.s listed in the literature range from >320°[4] to 342°[15]); *picrate*, orange-yellow needles, m. p. 268° (sublim. >345°), from ethanol (Found: N, 15·9. $C_{21}H_{13}N_5O_7$ requires N, 15·7%). The following hydrazones were similarly prepared: **1,2,3,4-*tetrahydro*-4-*oxo*-1-*toluene*-p-*sulphonylquinoline* p-*tolylhydrazone***, needles, m. p. 209°, from toluene (Found: C, 68·3; H, 5·7; N, 10·4. $C_{23}H_{23}N_3O_2S$ requires C, 68·1; H, 5·7; N, 10·4%); **2,3-*xylylhydrazone***, yellowish prisms, m. p. 174°, from ethanol (Found: C, 68·9; H, 6·1; N, 10·1. $C_{24}H_{25}N_3O_2S$ requires C, 68·7; H, 6·0; N, 10·0%); and **3,4-*xylylhydrazone***, microneedles, m. p. 176°, from toluene (Found: C, 68·3; H, 5·8%). Other carbolines (Table 1) were similary prepared.

TABLE 1

Substituted 11H-benzo[*a*]-γ-carbolines [a]

Substituent	M. p.	Formula	Found (%) C	H	N	Required (%) C	H	N
6-Methyl [b]	299°	$C_{16}H_{12}N_2$	(*M*, 232)		12·0	(*M*, 232)		12·1
Picrate	252 (decomp. >245)	$C_{22}H_{15}N_5O_7$	—	—	15·2	—	—	15·2
8-Methyl	308	$C_{16}H_{12}N_2$	82·4	5·5	12·2	82·7	5·2	12·1
Hemipicrate	258 (decomp. >235)	$C_{38}H_{27}N_7O_7$	—	—	14·2	—	—	14·1
9,10-Dimethyl	353	$C_{17}H_{14}N_2$	82·3	5·7	11·2	82·9	5·7	11·4
Dipicrate	208 (decomp. >170)	$C_{29}H_{20}N_8O_{14}$	—	—	16·1	—	—	15·9
8,9-Dimethyl	346	$C_{17}H_{14}N_2$	82·4	5·7	11·5	82·9	5·7	11·4
Picrate	306 (decomp. >280)	$C_{23}H_{17}N_5O_7$	—	—	14·5	—	—	14·7
6,8-Dimethyl	302	$C_{17}H_{14}N_2$	(*M*, 246)		11·3	(*M*, 246)		11·4
Picrate	265	$C_{23}H_{17}N_5O_7$	—	—	14·6	—	—	14·7
2-Chloro-6-methyl	323	$C_{16}H_{11}ClN_2$	72·3	4·3	10·3	72·0	4·1	10·5
Picrate	285 (decomp. >275)	$C_{22}H_{14}ClN_5O_7$	—	—	14·2	—	—	14·1
2-Chloro-6,8-dimethyl	325	$C_{17}H_{13}ClN_2$	(*M*, 280)		9·9	(*M*, 280·5)		10·0
Picrate	278 (decomp. >265)	$C_{23}H_{16}ClN_5O_7$	—	—	13·7	—	—	13·7
2-Methoxy [c]	322	$C_{16}H_{12}N_2O$	(*M*, 248)		11·7	(*M*, 248)		11·3
Picrate	290 (decomp. >275)	$C_{22}H_{15}N_5O_8$	—	—	15·0	—	—	14·7
2-Methoxy-8-methyl	317	$C_{17}H_{14}N_2O$	77·6	5·5	10·6	77·8	5·4	10·7
Picrate	298 (decomp. >280)	$C_{23}H_{17}N_5O_8$	—	—	14·2	—	—	14·3

[a] All these compounds were purified by sublimation at 230—260° *in vacuo* and crystallisation from methanol or aqueous ethanol; their addition compounds with picric acid were recrystallised from *o*-dichlorobenzene or nitrobenzene, and were bright yellow to orange-yellow needles. [b] Prepared by Kermack and Smith [16] through another route; they gave m. p. 298°. [c] Kermack and Storey [15] gave m. p. 315°.

13H-*Dibenzo*[a,i]-γ-*carboline* (III).—Obtained directly by spontaneous cyclisation in the course of the preparation of the α-naphthylhydrazone of ketone (I; R = R′ = H) from α-naphthylhydrazine hydrochloride and sodium acetate, this *indole* was purified by sublimation *in vacuo*, and formed colourless needles, m. p. 385° (sublim. >280°); u.v. absorption bands at 275 and 283 mμ, as compared with 280 (inflexion) and 289 mμ for 13*H*-dibenzo[*a*,*i*]carbazole (Found: C, 84·6; H, 4·8; N, 10·6. $C_{19}H_{12}N_2$ requires C, 85·1; H, 4·5; N, 10·4%); *picrate*, deep yellow prisms, m. p. 352°, from nitrobenzene (Found: N, 14·0. $C_{25}H_{15}N_5O_7$ requires N, 14·1%). The **2-*methoxy-derivative*** formed colourless needles, m. p. 322° (sublim. >280°), from benzene (Found: C, 80·5; H, 4·9; N, 9·3. $C_{20}H_{14}N_2O$ requires C, 80·5; H, 5·7; N, 9·4%)

[15] W. O. Kermack and N. E. Storey, *J.*, 1950, 607.
[16] W. O. Kermack and J. F. Smith, *J.*, 1930, 2002.

picrate, yellow needles, m. p. 334° (decomp. >305°) (Found: N, 13·3. $C_{26}H_{17}N_5O_8$ requires N, 13·3%). The 2-*chloro*-6-*methyl derivative* formed colourless, sublimable needles, m. p. 304°, from toluene (Found: N, 8·9%; *M*, 316. $C_{20}H_{13}ClN_2$ requires N, 8·8%; *M*, 316·5); *picrate*, m. p. 335° (decomp. >290°) (Found: N, 12·8. $C_{26}H_{16}ClN_5O_7$ requires N, 12·8%).

6-*Methyl*-13H-*dibenzo*[a,i]-γ-*carboline*.—A solution of the above chloro-compound (0·5 g.) in propan-2-ol (30 c.c.) was refluxed for 3 hr. with Raney nickel (1·5 g.); the catalyst was filtered off, the solvent removed, and the residue sublimed over 5% palladised charcoal, to give colourless prisms (70% yield), m. p. 295°, from methanol (Found: N, 9·8. $C_{20}H_{14}N_2$ requires N, 9·9%); *picrate*, orange-yellow prisms, m. p. 333° (decomp. >290°) (Found: N, 13·4. $C_{26}H_{17}N_5O_7$ requires N, 13·7%). All the other dehalogenations were performed in the same way and with similar yields.

13H-*Dibenzo*[a,g]-γ-*carboline* (IV).—1,2,3,4-*Tetrahydro*-4-*oxo*-1-*toluene*-p-*sulphonylquinoline* β-*naphthylhydrazone*, colourless prisms, m. p. 206°, from toluene (Found: C, 70·7; H, 5·2; N, 9·4. $C_{26}H_{23}N_3O_2S$ requires C, 70·7; H, 5·2; N, 9·5%) was cyclised to the *carboline* (IV), which sublimed as colourless prisms, m. p. 409° (Found: C, 84·9; H, 4·7; N, 10·5%); *dipicrate*, bright yellow prisms, m. p. 305° (decomp. >270°) (Found: N, 15·3. $C_{31}H_{18}N_8O_{14}$ requires N, 15·4%). The 2-*methoxy-derivative* formed colourless needles, m. p. 365° (sublim. >310°) (Found: N, 9·2%); *picrate*, orange-yellow prisms, m. p. 305° (decomp. >285°) (Found: N, 13·3%).

2-*Chloro*-6-*methyl*-13H-*dibenzo*[a,g]-γ-*carboline*.—The β-*naphthylhydrazone* of ketone (I; R = Me, R′ = Cl), yellowish prisms, m. p. 180°, from benzene (Found: C, 71·6; H, 5·3. $C_{20}H_{18}ClN_3$ requires C, 71·5; H, 5·4%) gave, on cyclisation, a *carboline* which crystallised as colourless needles, m. p. 296° (sublim. >245°), from ethanol (Found: N, 8·6%; *M*, 316); *picrate*, orange-yellow needles, m. p. 311° (decomp. >280°) (Found: N, 12·8%). The 6-*methyl derivative*, obtained by dechlorination, formed colourless prisms, m. p. 355° (sublim. >270°), from chlorobenzene (Found: C, 85·0; H, 5·0; N, 10·1. $C_{20}H_{14}N_2$ requires C, 85·1; H, 5·0; N, 9·9%); *picrate*, deep yellow needles, m. p. 271° (decomp. >250°) (Found: N, 13·4%).

7H-*Benzo*[a]*pyrido*[3,2-g]-γ-*carboline* (V).—Prepared from 6-quinolylhydrazine and ketone (I; R = R′ = H), this *compound* formed colourless microprisms, m. p. 389° (sublim. >290°), from aqueous ethanol (Found: C, 79·8; H, 4·4; N, 15·7. $C_{18}H_{13}N_3$ requires C, 80·3; H, 4·1; N, 15·6%); picrate, deep yellow prisms, m. p. 245° (decomp. >220°).

11H-*Pyrido*[2,3-i]-γ-*carboline* (VII).—*N*-Benzyl-4-piperidone 5-quinolylhydrazone was cyclised in the usual way, to give compound (VI), which was not purified, and which was sublimed over palladised charcoal to give the *carboline* (VII), as colourless needles, m. p. 287° (sublim. >230°), from ethanol; this compound repeatedly did not give satisfactory carbon and hydrogen analyses, but its structure was ascertained by mass spectrometry (Found: N, 18·8%; *M*, 219. $C_{14}H_9N_3$ requires N, 19·2%; *M*, 219).

Attempted Synthesis of 7H-*indeno*[2,1-c]*quinoline* (VIII).—Equimolar amounts of benzaldehyde and ketone (I; R = R′ = H) were dissolved in the minimum of a 4% solution of potassium hydroxide in ethanol, and the solution stirred for 10 min. then left overnight at room temperature;[17] the solid precipitate obtained in 70% yield was recrystallised from methanol, giving 3-*benzylidene*-1,2,3,4-*tetrahydro*-4-*oxoquinoline*, straw-coloured leaflets, m. p. 210°, whose halochromy in sulphuric acid was orange-yellow (Found: C, 81·6; H, 5·6; N, 6·0. $C_{16}H_{13}NO$ requires C, 81·7; H, 5·5; N, 6·0%). Heating this compound with polyphosphoric acid for 3 hr., at 120, 140, and 150°, did not induce cyclodehydration; similar failures have been recorded with the condensation products of 1-tetralone with pyridine- and quinoline-aldehydes.[18] Borsche and Sinn [19] prepared compound (VIII) by reduction of the corresponding 7-oxo-compound.

Pfitzinger Reactions with Ketones (I).—These were effected as usual with the appropriate isatin, in a 20% solution of potassium hydroxide in ethanol. The cinchoninic acids obtained were purified, either by crystallisation from acetic acid to give yellow prisms, or *via* their sodium salts; they were not analysed, but were directly decarboxylated by heating above their m. p. The naphthyridines obtained (Table 2) were recrystallised from methanol, ethanol, or aqueous ethanol, to give sublimable, colourless or pale yellow needles, whose halochromy in sulphuric acid ranged from greenish-yellow to orange; the yellow picrates were recrystallised from

[17] Cf. N. P. Buu-Hoï, O. Roussel, and P. Jacquignon, *Bull. Soc. chim. France*, 1964, 3097.
[18] G. Saint-Ruf, N. P. Buu-Hoï, and P. Jacquignon, *J.*, 1960, 2690.
[19] W. Borsche and F. Sinn, *Annalen*, 1939, **538**, 283.

TABLE 2

Dibenzo[*b*,*h*][1,6]naphthyridines

Substituent	M. p.	Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
5,6-Dihydro [a]	245°	$C_{16}H_{12}N_2$						
Picrate	259 (decomp. >230)	$C_{22}H_{15}N_5O_7$	—	—	15·1	—	—	15·2
Compound (IX) [b]	186	$C_{16}H_{10}N_2$						
Picrate	230 (decomp. >210)	$C_{22}H_{13}N_5O_7$	—	—	15·2	—	—	15·3
7-Carboxy-5,6-dihydro	246 (decomp. >205)	$C_{18}H_{14}N_2O_2$						
5,6-Dihydro-9-methyl	229	$C_{17}H_{14}N_2$	82·6	5·6	11·1	82·9	5·7	11·4
Picrate	245 (decomp. >230)	$C_{23}H_{17}N_5O_7$	—	—	14·2	—	—	14·7
9-Methyl	164	$C_{17}H_{12}N_2$	83·4	5·1	11·7	83·6	4·9	11·5
Picrate	244 (decomp. >225)	$C_{23}H_{15}N_5O_7$	—	—	14·7	—	—	14·8
7-Carboxy-5,6-dihydro-9,10-dimethyl	289 (decomp. >240)	$C_{19}H_{16}N_2O_2$						
9,10-Dimethyl [c]	203	$C_{18}H_{14}N_2$	83·4	5·7	10·9	83·7	5·4	10·9
Picrate	243 (decomp. >215)	$C_{24}H_{17}N_5O_7$	—	—	14·5	—	—	14·4
7-Carboxy-5,6-dihydro-9,11-dimethyl	225	$C_{19}H_{16}N_2O_2$						
9,11-Dimethyl [d]	177	$C_{18}H_{14}N_2$	83·5	5·6	10·8	83·7	5·4	10·9
Picrate	268 (decomp. >250)	$C_{24}H_{17}N_5O_7$	—	—	14·7	—	—	14·4
7-Carboxy-9-chloro-5,6-dihydro [e]	230 (decomp. >180)	$C_{17}H_{11}ClN_2O_2$						
7-Carboxy-2-chloro-5,6-dihydro-6-methyl [f]	185 (decomp. >150)	$C_{18}H_{13}ClN_2O_2$						—
2-Chloro-6-methyl [g]	183	$C_{17}H_{11}ClN_2$	73·0	4·3	10·1	73·2	3·9	10·1
Picrate	260 (decomp. >225)	$C_{23}H_{14}ClN_5O_7$	—	—	13·7	—	—	13·8
2-Chloro-6,9-dimethyl	222	$C_{18}H_{13}ClN_2$	73·6	4·6	9·3	73·8	4·4	9·6
Picrate	273 (decomp. >245)	$C_{24}H_{16}ClN_5O_7$	—	—	13·2	—	—	13·4
6-Methyl [h]	140	$C_{17}H_{12}N_2$						
6,9-Dimethyl	168	$C_{18}H_{14}N_2,H_2O$	—	—	9·4	—	—	9·5
Picrate	212 (decomp. >180)	$C_{24}H_{17}N_5O_7$	—	—	14·5	—	—	14·4
7-Carboxy-5,6-dihydro-2-methoxy	260 (decomp. >220)	$C_{18}H_{14}N_2O_3$						
2-Methoxy	159	$C_{17}H_{12}N_2O$	78·5	4·8	10·8	78·5	4·6	10·8
Picrate	236 (decomp. >225)	$C_{23}H_{15}N_5O_8$	—	—	14·2	—	—	14·3
7-Carboxy-5,6-dihydro-2-methoxy-9-methyl	278 (decomp. >230)	$C_{19}H_{16}N_2O_3$						
5,6-Dihydro-2-methoxy-9-methyl	256	$C_{18}H_{16}N_2O$,EtOH	74·5	6·9	8·7	74·5	6·8	8·7
Picrate	282 (decomp. >238)	$C_{24}H_{19}N_5O_8$	—	—	13·8	—	—	13·9
2-Methoxy-9-methyl [i]	175	$C_{18}H_{14}N_2O$	78·7	5·0	10·2	78·8	5·1	10·2
Picrate	264 (decomp. >250)	$C_{24}H_{17}N_5O_8$	—	—	13·8	—	—	13·9

[a] Lit.,[4] m. p. 237°. [b] U.v. absorption bands at 222 and 278 mμ (benz[*c*]acridine: 224, 280, and 290 mμ); lit.,[4] m. p. 186°. [c] *M* (found by mass spectrometry), 258. Calc., 258. [d] Molecular peak at 258. [e] Underwent decomposition on attempted decarboxylation. [f] Crystallised from acetone as red prisms. [g] Molecular peak at 278. [h] Lit.,[11] m. p. 137°. [i] U.v. absorption bands at 224, 278, and 300 mμ.

chlorobenzene, *o*-dichlorobenzene, or nitrobenzene. Where a dihydro-base was obtained, dehydrogenation was effected with palladised charcoal.

We thank Mrs. C. Orley for the mass spectrograms (taken on an Atlas CH 4 apparatus at 70 ev and 40mA; ionisation temperature, 280°), and the "Comite Cancer et Leucemie" (Professor R. Latarjet) of the French Government for a Research Fellowship to one of us (O. R.).

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