Anal. Calcd. for $C_{22}H_{42}BrN_2O$: C, 52.52; H, 8.29; Br, 31.31; N, 5.49. Found: C, 52.57; H, 8.48; Br, 31.20; N, 5.41.

In each of the three instances in which I was prepared, using identical reaction conditions, yields of 42%, or in excess thereof, were obtained.

Diethiodide of the Bis(2-ethyldecahydroisoquinoline) Ether (II).—The diethiodide derivative (II) of the above basic ether (I) was prepared by refluxing the free base, obtained from the neutralization of 1.0 g. of the bis(2-ethyldecahydroisoquinoline) ether dihydrobromide, dissolved in 25 ml. of dry benzene, for 4 hr. with excess ethyl iodide. The precipitated quaternary iodide was filtered and recrystallized from an alcohol–ether mixture to yield 0.93 g. (72%) of fine white needles, m.p. 245.0–245.4°. The infrared spectrum (KBr) showed a medium intensity absorption band at 1110 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{50}I_2N_2O$: C, 47.28; H, 7.63; I, 38.43; N, 4.24. Found: C, 47.28; H, 7.40; I, 38.20; N 4.27.

Acknowledgment.—The author is indebted to Marion Laboratories, Inc., Kansas City, Missouri, for their financial assistance in support of this project and also to Dr. A. Lasslo for his useful discussions and interest in the work.

6-Phenyltetrahydroquinoline

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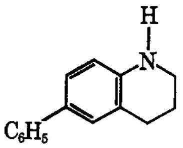
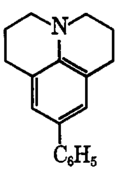
In 1885, LaCoste and Sorger[2] claimed to have prepared 6-phenyltetrahydroquinoline (I) by the reduction of 6-phenylquinoline with zinc and hydrochloric acid. They reported that the compound was unstable and that it was soluble in hot water but insoluble in chloroform and benzene. The only other reference to this compound appears to be in 1957 when Avramoff and Sprinzak[3] suggested that the instability claimed above might explain their failure to isolate the compound, as its picrate, on reduction of 6-phenylquinoline under conditions that gave 8-phenyltetrahydroquinoline from 8-phenylquinoline.



I



II

We have now prepared an authentic sample of the compound by the acid-catalyzed thermal decomposition[4,5] of N,N′-(*p*-biphenyl)-1,3-diaminopropane. It is a colorless crystalline solid, m.p. 79.5°, insoluble in hot water and freely soluble in benzene and chloroform. The infrared spectrum and elemental analyses are in accord with the structure. The compound seems as stable as similar tetrahydroquinolines, showing only a slight tendency to darken on exposure to air and light. It gives a picrate, m.p. 204°, and a benzoyl derivative, m.p. 142°, in contrast to LaCoste and Sorger's values of 165 and 137°, respectively. There seems little doubt that these workers had, at best, a very impure sample of the original compound.

The previously unreported 9-phenyljulolidine (II) was also obtained in the decomposition as expected.[4]

Experimental Section[6]

N,N′-Bis(*p*-biphenyl)-1,3-diaminopropane.—A solution of *p*-aminobiphenyl[7] (47.5 g.) and 1,3-dibromopropane (14.0 g.) in 70 ml. of benzene was refluxed for a total of 20 hr. The precipitated amine hydrobromides were twice removed during this time by adding 400 ml. of benzene and then washing with 10% aqueous sodium hydroxide solution before reducing the volume by distillation. The mixture was finally washed with aqueous alkali and with water and dried (K_2CO_3), and the excess *p*-aminobiphenyl (23.2 g.) was removed by distillation, b.p. 152–154° (1 mm.). The required compound was obtained as a yellow solid (10.2 g., 39%), b.p. 300–310° (0.5 mm.). It was washed with a little ether and then recrystallized from ethanol to give 7.5 g. of material, m.p. 111°.

Anal. Calcd. for $C_{27}H_{26}N_2$: C, 85.68; H, 6.92; N, 7.40. Found: C, 85.62; H, 7.06; N, 7.41.

6-Phenyltetrahydroquinoline. A.—The diaminopropane above (6.0 g.) was decomposed at 260–270° in the presence of 0.2 ml. of 48% hydrobromic acid by the method previously described.[4] An ethereal solution of the resultant distillate (5.0 g.) was washed with aqueous alkali and with water and the primary aromatic amines then removed by treatment[8] with 50% aqueous zinc chloride solution (2.52 g. of *p*-aminobiphenyl was recovered from the complex obtained). Distillation of the ethereal solution gave 1.0 g. (31%) of 6-phenyltetrahydroquinoline (b.p. 210–220° at 20 mm.).

B.—In a second preparation the intermediate diaminopropane was not isolated. *p*-Aminobiphenyl (60 g.), 1,3-dibromopropane (18 g.), and anhydrous potassium carbonate (18 g.) were heated together at 160° for 5 min. The mixture was then cooled and extracted by shaking with ether and water. The excess *p*-aminobiphenyl (32.5 g. recovered) was removed from the ether layer by shaking with aqueous zinc chloride solution. The crude diamine obtained after evaporation of the ether was decomposed as above and the *p*-aminobiphenyl formed was removed. Distillation then afforded the crude 6-phenyltetrahydroquinoline (4.1 g.), b.p. 150–189° (1 mm.). [The next fraction (3.0 g.), b.p. 190–192° at 1 mm., was 9-phenyljulolidine.] Redistillation gave the tetrahydroquinoline (2.2 g.) as an oil, b.p. 154–164° (1 mm.), which gradually solidified.

The 6-phenyltetrahydroquinoline was recrystallized from petroleum ether (b.p. 60–80°) to give colorless crystals, m.p. 79.5°. The infrared spectrum (melt) showed peaks at 3415 (N–H), 892 (isolated C_{Ar}–H), 825 (two adjacent C_{Ar}–H bonds), 761 and 698 cm.$^{-1}$ (monosubstituted benzene).

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.90; H, 6.98; N, 6.55.

The compound gave a benzoyl derivative, m.p. 142° from aqueous ethanol.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.21; H, 6.02; N, 4.57.

It also gave a picrate, m.p. 203–204°.

Anal. Calcd. for $C_{21}H_{18}N_4O_7$: N, 12.78. Found: N, 12.85.

The 9-phenyljulolidine was recrystallized from petroleum ether to give colorless crystals, m.p. 69° (sharply depressed by addition of 6-phenyltetrahydroquinoline). The infrared spectrum had no peaks in the ranges 3600–3400 and 850–800 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.51; H, 7.68; N, 5.41.

It gave a methiodide, m.p. 210°.

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[1] School of Chemical Sciences, University of East Anglia, Norwich, England.

[2] W. LaCoste and C. Sorger, *Ann.*, **230**, 1 (1885).

[3] M. Avramoff and Y. Sprinzak, *J. Org. Chem.*, **22**, 571 (1957).

[4] G. B. Russell, G. J. Sutherland, R. D. Topsom, and J. Vaughan, *ibid.*, **27**, 4375 (1962).

[5] I. K. Lewis, G. B. Russell, R. D. Topsom, and J. Vaughan, *ibid.*, **29**, 1183 (1964).

[6] Analyses were by the microanalytical laboratories at the University of Otago (Dr. A. D. Campbell) and Drs. G. Weiller and F. B. Strauss, Oxford. Infrared spectra were determined with a Perkin-Elmer 237 spectrometer.

[7] This compound is considered to be a dangerous carcinogen: private communication from Dr. R. A. M. Case, Chester Beatty Research Institute, London.

[8] See footnote 35 of ref. 5.

Anal. Calcd. for $C_{19}H_{22}IN$: C, 58.32; H, 5.67; N, 3.58. Found: C, 58.40; H, 5.67; N, 3.64.

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The Chemical Examination of *Iris nepalensis.* III. Isolation and Structure of Irisolidone

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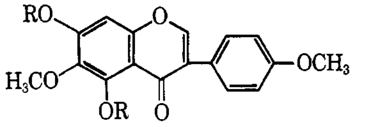
Isolation of irisolone[1] and irigenin[2] from the rhizomes of *Iris nepalensis* D. Don (*Iridaceae*) has been reported earlier. Petroleum ether extracts of plants do not usually contain flavonoids[3] but here an examination of this extract indicated the presence of a new isoflavone in 0.01% yield. This has been characterized as 5,7-dihydroxy-6,4′-dimethoxyisoflavone (I, R = H) and named irisolidone.

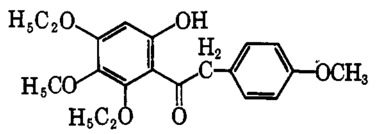


I

Irisolidone gave the characteristic color reactions of isoflavones. Its infrared spectrum showed strong absorption in the 6–6.6-μ region usually associated with flavonoid systems,[4] and the ultraviolet absorption spectrum was similar to that of irisolone and tri-O-methyltectorigenin.

Irisolidone showed correct analysis for $C_{17}H_{14}O_6$ and two methoxyl groups. Color with ferric chloride and formation of diacetate, dimethyl ether, and a diethyl ether (I, R = Ac, CH_3, and C_2H_5, respectively) showed the presence of two free hydroxyl groups in the molecule. Specific color reactions further indicated that one of these must be located in the 5-position and that vicinal hydroxyl groups were not present. A bathochromic shift of 10 mμ in the ultraviolet spectrum characteristic of 5-hydroxyl was observed on addition of aqueous aluminum chloride[5,6] and a similar shift of 5 mμ on addition of fused sodium acetate suggested a 7-hydroxyl. Though a shift of 10 mμ[7] is usually associated with the presence of 7-hydroxyl, Gottlieb and Magalhaes have recently reported a shift of only 8 mμ for caviunin.[4]

Irisolidone dimethyl ether was identical with tri-O-methyltectorigenin. This along with the formation of antiarol and anisic acid on alkali fusion of the dimethyl ether established the substitution pattern for irisolidone which was confirmed by the alkaline degradation of diethyl ether first to the deoxybenzoin (II) and then to 3,5-diethoxy-4-methoxyphenol and anisic acid.



II

Comparison of authentic 5,7-dihydroxy-6,4′-dimethoxyisoflavone[8] (mixture melting point and infrared spectrum) with irisolidone showed the two to be identical.

A number of species belonging to *Iridaceae* have been examined for isoflavonoids and as a result of this it is possible to make some observations regarding their biogenesis and chemical taxonomy which may be of significance.

Thus it is interesting that all the isoflavonoids so far reported from this family have tectorigenin substitution pattern in ring A, as indicated in Table I.

TABLE I

Plant	Isoflavonoid	Substitution in ring A	Substitution in ring B
I. florentina *I. kumaonensis* *I. germanica*	Irigenin	5-OH 6-OCH_3 7-OH	3′-OH 4′-OCH_3 5′-OCH_3
I. tectorum	Tectorigenin	5-OH 6-OCH_3 7-OH	4′-OH
I. nepalensis	Irisolone	5-OCH_3 $^{6\text{-O}}_{7\text{-O}}{>}CH_2$	4′-OH
	Irisolidone	5-OH 6-OCH_3 7-OH	4′-OCH_3
	Irigenin	5-OH 6-OCH_3 7-OH	3′-OH 4′-OCH_3 5′-OCH_3

With respect to the substitution pattern of ring B the above members of *Iridaceae*, with the exception of *I. tectorum*, elaborate isoflavones with oxygen functions at the 3′-, 4′-, and 5′-positions. *I. tectorum*, on the other hand, produces tectorigenin which carries only a 4′-hydroxyl. *I. nepalensis* contains both types of isoflavonoids and thus appears genetically related to the two. Further, all isoflavonoids from *Iridaceae* have a 6-methoxyl, with the exception of irisolone which has a 6,7-methylenedioxy group. Formation of this may involve an oxidative cyclization of the methoxyl as suggested by Barton[9] in connection with the biogenetic origin of the methylenedioxy group in alkaloids, etc.

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