SHORT COMMUNICATIONS

Pakistan J. Sci. Ind. Res., **12**, 153–154 (1969)

A CONTRIBUTION TO THE PHARMACOGNOSTIC STUDY OF THE FRUIT OF SCHNIUS MOLLE L.

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Schinus molle L., an ever green tree of the family Anacardiaceae, is naturalized and cultivated in the northern region of West Pakistan. Its fruit and oil are used as an adulterant and a substitute for those of *Piper nigrum*[1] to which it closely resembles morphologically as well as in physical and chemical characters. Keeping in view its economic importance a preliminary investigation of its pharmacognosy has been undertaken. The plant material, collected from the experimental farm, was fixed for 12 hr in a solution of Formalin–acetic acid–ethanol in a ratio of 1:1:18 and dehydrated by normal butanol and ethanol. Microtome sections were prepared after usual embedding in paraffin and staining in safranin and fast green. The maceration of the tissue was done according to Jaffery[2] and hand sections were cut for the microchemical test after Johansen and Gurr.[3]

Description of the Fruit

The drupe is globose, 0.2 in. in dia, green when fresh turning to red on maturity. It comprises three layers namely (a) *epicarp*, (b) *mesocarp*, and (c) *endocarp*. The *Epicarp*, which is the outer most layer, consists of (a) *epidermis* (single layer of polygonal cells, measuring 21.4–27.1–28.61μ in length and 14.3–24.3–28.6μ in breadth) and (b) hypodermis (2-3 layers of thick welled cells). The *mesocarp* is made up of thin walled parencymatous cells, measuring 42.3–51.3–57.2μ in length and 41.9–50.8–57.2μ in breadth, and contain oil globules scattered among the cells. It is followed by a layer of ovoid cells having oil globules and is known as the oil layer. The *endocarp* is formed of thick walled elongated, sclerenchymatous cells and is followed by colourless oval cells of hyaline layer (Fig. 1). The *seed coat* contains elongated, sclerenchymatous cells which are 100.1–185.4–243.0μ in length and 14.3–21.6–28.6μ in breadth.

Powder Drug

The powder of the fruit is brown in colour having pungent smell and acrid taste. The non-glandular

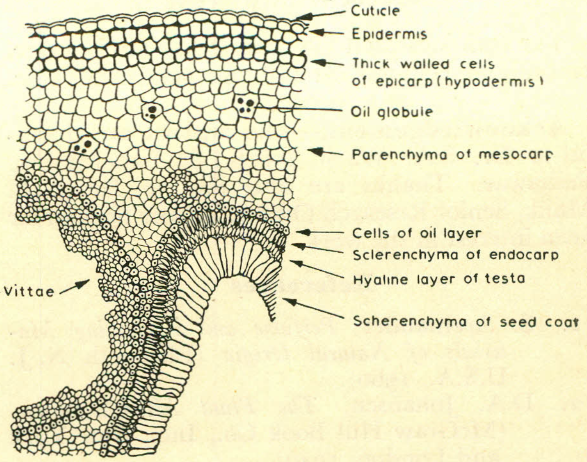

Fig. 1.—T.S. of fruit of schinus molle (Mag.×80).

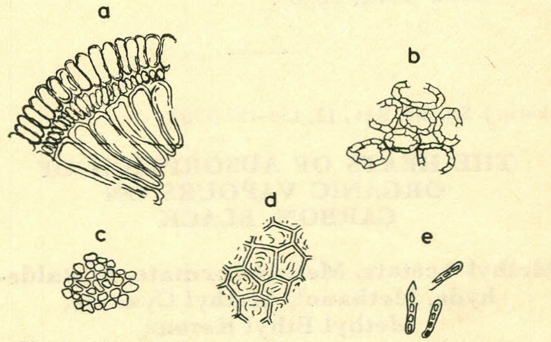

Fig. 2.—Powdered fruit of schinus molle (Mag.×80). (a) Cells of endocarp, colourless layer of testa and seed coat, (b) Thick walled porous cells of testa, (c) Parenchyma of mesocarp, (d) Epidermal cells of epicarp and (e) Uniseriate trichomes.

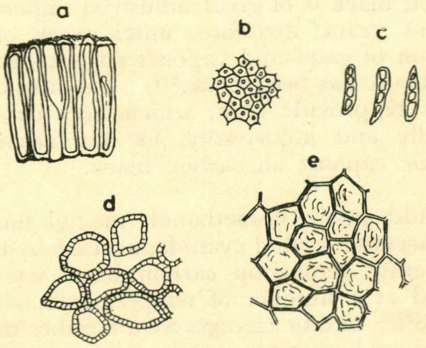

Fig. 3.—Macerate of fruit of schnius molle (Mag.×80). (a) Cells of seed coat, (b) Colourless crystal bearing cells of testa, (c) Uniseriate non-grandular trichomes, (d) Thick walled porous cells of testa and (e) Epidermal cells of epicarp.

hairs and thick walled cells of testa (Figs. 2 and 3) were observed apart from parenchymatous and sclerenchymatous cells of *mesocarp* and *endocarp*, respectively.

Microchemical Test

The fruit indicated the presence of starch, sugar, chitin and cellulose in the microchemical tests.

Acknowledgement.—The authors are thankful to Dr. S.A. Warsi, P.C.S.I.R. Laboratories, Peshawar. Thanks are also due to Dr. N.A. Malik, Senior Research Officer, Botany Section for keen interest in the work.

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THE HEATS OF ADSORPTION OF ORGANIC VAPOURS ON CARBON BLACK

Methyl Acetate, Methyl Formate, Acetaldehyde, Methanol, Methyl Cyanide, Methyl Ethyl Ketone

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Carbon black is of great industrial importance. In recent years, therefore, much work on the adsorption of gases and vapours on graphite and carbon black has been done.[1,2] The aim of this paper is to provide data, which may be useful chemically and industrially, for the adsorption of organic vapours on carbon black.

The adsorption of methanol, methyl formate, methyl acetate, methyl cyanide, acetaldehyde and methyl ethyl ketone on carbon black has been measured at a number of temperatures between 0 and 40°C, and ΔH changes at a number of temperatures and coverages from the resulting adsorption isotherms using the Clausius–Clapeyron equation have been calculated.

The specific surface area of the solid was computed using the BET method[3] from the adsorption data of nitrogen on carbon black at the liquid air temperature.

Apparatus and Procedure

The apparatus used for the adsorption of organic vapours on carbon black was of the volumetric type,[4] with some modifications. The whole system was connected to the main vacuum line through a large dia. (23 mm) manifold. For pressure measurements Pirani and ionization gauges were used. The Pirani gauge gave an estimate of pressure down to 10^{-3} mm, while below this the ionization gauge was used to 10^{-5} mm. All the joints in the vacuum system were quickfit B14. The main manifold was connected to a 2-in mercury diffusion pump backed by a rotary oil pump through a B54 joint.

Results

The surface area measurement by the BET method gave a value of 74.02 m^2g^{-1}. The heats of adsorption were calculated from a series of isotherms by using the Clausius–Clapeyron equation in the form

$$qst = \frac{2.303\, R \log P_2/P_1}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

where R, gas constant in cal $mole^{-1}$ deg^{-1}; P_1, pressure of adsorbate at T_1, and pressure P_2 at temperature T_2; and qst, isosteric heat of adsorption at constant coverage.

qst calculated from the above equation, however, is not the same as ΔH for the adsorption process. The relation between these quantities has been given by Hill.[5]

Values of qst in kcal $mole^{-1}$ are summarized in Tables 1-6.

TABLE 1.—HEAT OF ADSORPTION OF METHYL ACETATE.

Coverage	27.5°	30°
2 ml	25.62	20.96
3 ml	20.02	19.56
5 ml	12.89	33.61

TABLE 2.—HEAT OF ADSORPTION OF METHYL FORMATE.

Coverage	15°	30°	35°
2 ml	10.87	11.02	12.51
4 ml	9.18	7.50	6.91
6 ml	5.26	10.00	16.54

TABLE 3.—HEAT OF ADSORPTION OF ACETALDEHYDE.

Coverage	15°	27.5°
1.5 ml	7.50	10.76
2.5 ml	14.18	53.59

TABLE 4.—HEAT OF ADSORPTION OF METHANOL.

Coverage	27.5°	30°	37.5°
2 ml	9.17	10.74	13.58
5 ml	9.17	9.99	20.71
9 ml	9.75	10.03	31.83
13 ml	9.60	—	—

TABLE 5.—HEAT OF ADSORPTION OF METHYL CYANIDE.

Coverage	27.5°	32.5°
2 ml	5.54	10.93
4 ml	6.82	8.17
7 ml	7.39	7.66
9 ml	4.08	8.16

TABLE 6.—HEAT OF ADSORPTION OF METHYL ETHYL KETONE.

Coverage	27.5°	32.5°
2 ml	8.48	—
5 ml	8.43	11.60
10 ml	6.22	5.45
13 ml	5.13	1.74

Discussion

The majority of the organic compounds used for adsorption on carbon black gave sigmoid or type 2 isotherms (Figs. 1–6). All these isotherms indicate a multimolecular adsorption and a greater value of the heat of adsorption for the first layer than for the layer above the first.[6]

An estimate of how the heat of adsorption will vary with temperature may be obtained from the Kirchoff equation.

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_P (T_2 - T_1)$$

The above equation indicates that if $T_2 - T_1$ is of the order of 10°, the value of ΔC_P for a system is not likely to exceed a few calories per mole and hence the total value of the term will not exceed 200 calories in any case.

The ΔH changes obtained at different temperatures in our experiments, therefore, indicate that the nature and the extent of surface interactions change with variations in temperature.

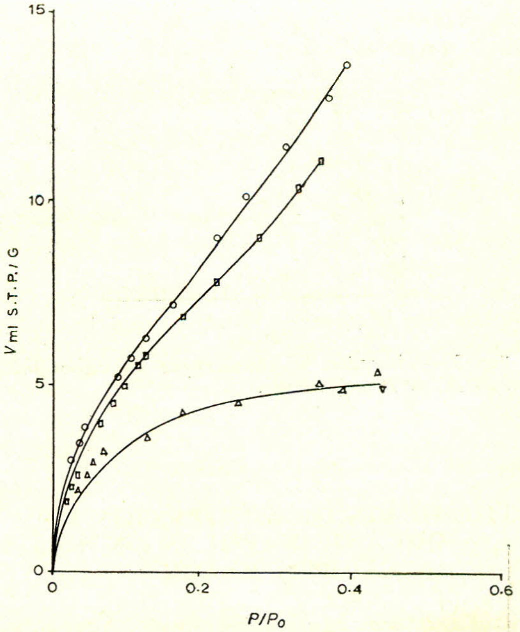

Fig. 1.—Adsorption of methyl acetate on carbon black. O at 25°, □ at 30°, Δ at 35°.

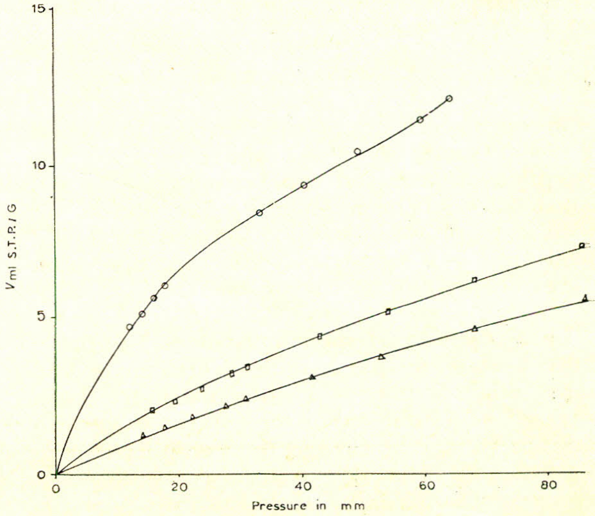

Fig. 2.—Adsorption of methyl formate on carbon black. O at 0°, □ at 25°, Δ at 35°.

Fig. 3.—Adsorption of acetaldehyde on carbon black. O at 0°, □ at 25′, △ at 30°.

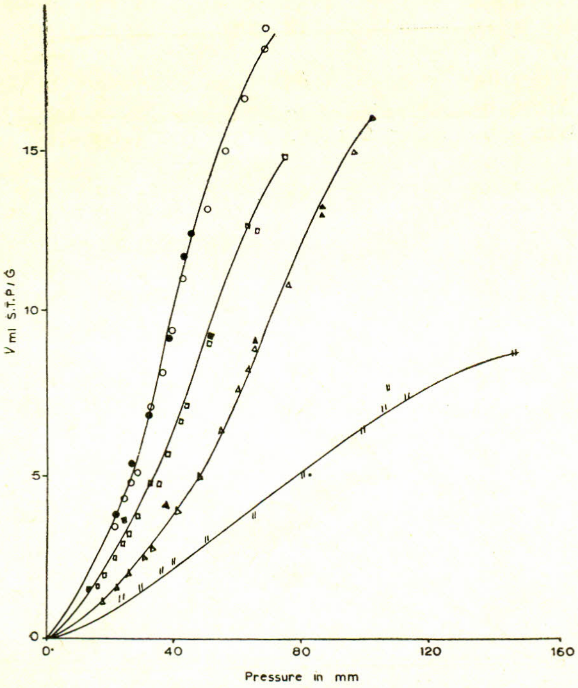

Fig. 4.—Adsorption of methanol on carbon black. O at 25°, at 30°, △ at 35°, || at 40°.

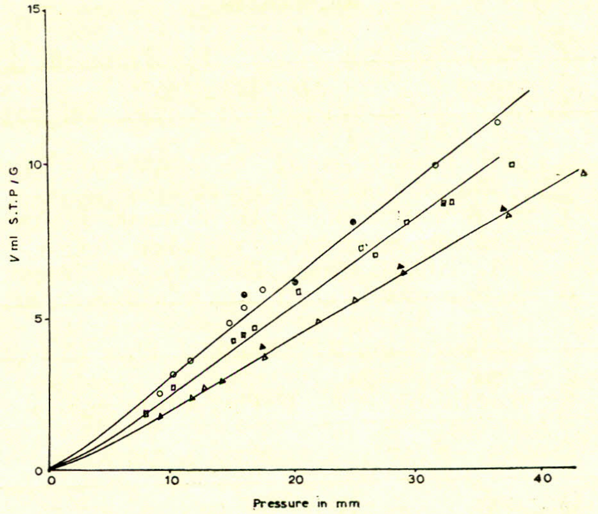

Fig. 5.—Adsorption of methyl cyanide on carbon black. O at 25°, □ at 30°, △ at 35°.

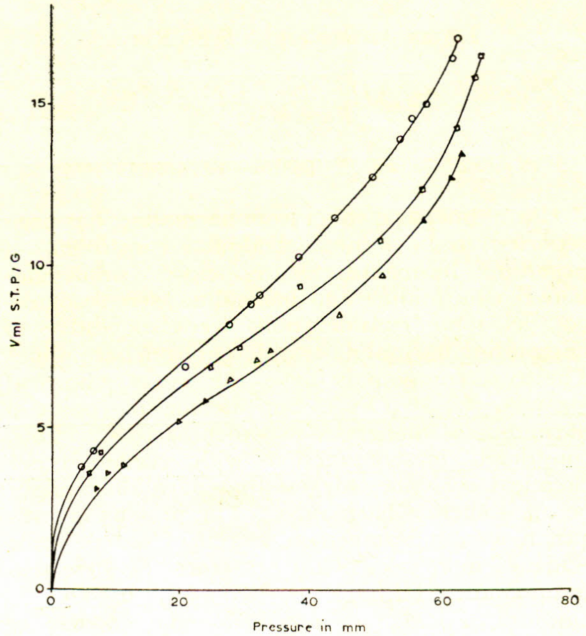

Fig. 6.—Adsorption of methyl ethyl ketone on carbon black. O at 25°, □ at 30°, △ at 35°. Solid points indicate description.

Pierce and Smith[7] have reported the isosteric heats of adsorption for methanol–graphite system. The heats of adsorption obtained at coverages comparable to those used in the present work gave values of 9.5 to 10 kcal mole^{-1} at 0°, which agree well with our value. Millard *et al.*[8] have carried out calorimetric studies for the methanol–carbon black system and confirm the observations of Pierce and Smith.

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X-RAY DATA OF HARMIDINE

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Harmidine, as distinct from harmaline, has been reported to be a new alkaloidal constituent of peganum harmala.[1] Many close similarities between harmidine and harmaline were recognised, yet some considerations were suggestive of designating harmidine as different from harmaline[1] The two compounds have the same empirical formula ($C_{13}H_{14}ON_2$), but the melting point of harmidine is higher by as much as 18°C. This, considered in conjunction with certain other chemical evidence, suggest that harmidine might be an isomer of harmaline. The present investigation was undertaken in search of independent evidence in respect of the structures of these two compounds. Through the courtesy of Dr. S. Siddiqui, F.R.S., we received some crystals of harmidine for X-ray studies. Some of these crystals were fairly large, measuring in some cases even a few millimeters in length, the lengthwise direction forming a well-developed zone axis (this axis we have designated as the c-axis of the crystal). The X-ray powder photographs of these crystals were taken with a 11.4 cm dia powder camera using filtered Cr K α radiation. The powder photograph was taken soon after having received the sample in order to avoid its being exposed to the atmosphere for any longer period. The photograph, thus obtained, is reproduced in Fig. 1, alongside of which are also reproduced the X-ray powder photographs of harmaline and harmine for comparison. In Table 1 are given the X-ray powder data of harmidine which were obtained from the X-ray photograph reproduced in Fig. 1. The powder data of harmaline and harmine, as given in Table 1, have been taken from published literature:[2] these data are in agreement with our own and thus provide a check on the samples of harmaline and harmine as used for taking the X-ray photographs given in Fig. 1.

TABLE 1.—COMPARISON OF THE X-RAY POWDER DATA OF HARMIDINE, HARMALINE AND HARMINE. THE ASTERISK MARKS INDICATE THE EXTRA LINES ON THE PATTERN OF HARMIDINE WHICH ARE NOT OBSERVED ON THAT OF HARMALINE.

Harmidine		Harmaline		Harmine	
I/I_0	d in Å			8.57	(32)
F	7.2	6.72	(7)	6.74	(12)
W	6.6	6.57	(13)		
W	6.2	6.17	(7)	6.09	(4)
S	5.6	5.58	(100)		
F	5.4	5.36	(7)	5.31	(32)
W	5.0*			4.99	(60)
				4.83	(100)
S	4.54	4.54	(100)	4.43	(100)
F	4.15	4.18	(7)	4.30	(32)
W	4.0*			3.93	(60)
VF	3.85	3.85	(7)	3.84	(60)
MS	3.8				
MS	3.6	3.63	(53)	3.69	(8)
F	3.57*				
MS	3.44	3.42	(27)	3.46	(40)
				3.38	(4)
F	3.24	3.21	(13)	3.21	(60)
MS	3.15	3.13	(33)	2.93	(16)
F	2.87	2.86	(3)	2.885	(4)
F	2.81	2.80	(3)	2.774	(8)
F	2.68	2.66	(3)		
F	2.64	2.61	(7)	2.623	(8)
F	2.55	2.55	(3)	2.568	(4)
F	2.46*				
F	2.42*				
F	2.37	2.35	(3)	2.413	(12)
F	2.30	2.29	(7)	2.318	(4)
F	2.25	2.24	(3)	2.256	(4)
F	2.21*				
F	2.16	2.14	(3)	2.147	(8)

Note: The figures within brackets indicate the intensities. S=Strong; MS=medium strong; W=Weak; F=Faint; V.F.=Very faint.

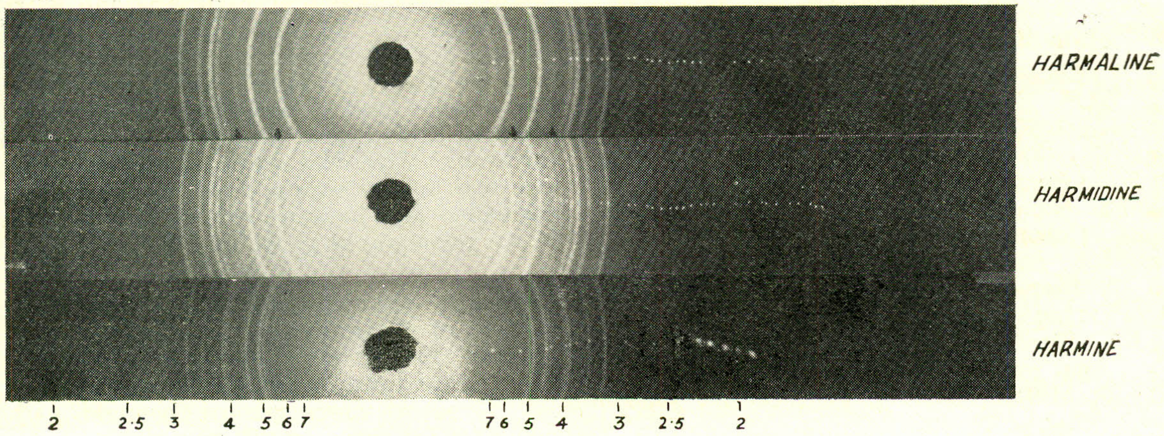

Fig. 1.—Comparison of the powder photographs of harmaline, harmidine and harmine.

Referring to Fig. 1 one may observe a striking correspondance between the patterns of harmidine and harmaline, with however one difference: that the pattern of harmidine shows two quite prominent extra lines (marked ↓) corresponding to d-values of 5.0Å and 4.0Å. On repeating the harmidine pattern with different samples it was observed that on some of these patterns, these lines were not very clearly visible; nevertheless one could still see faint diffuse regions corresponding to these lines. These lines do not seem to correspond with the lines of the harmine pattern either, thus ruling out the possibility of their arising due to any possible decomposition of harmidine into harmine. The presence of these extra lines suggests either one of two posibilities: (a) that the two compounds are identical and that the extra lines arise due to some impurities, (b) that harmidine is an isomer of harmaline, so that the two closely resembling kind of molecules may well be accomodated in the unit cell without substantially affecting the crystal structure; such a structure may under different conditions of crystallisation give a few extra lines due to a kind of super-structure.

Single crystal data of harmidine were also collected. The unit cell is orthorhombic; the cell dimensions, with estimated limits of error, are:

a =7.61 ±0.03A°,
b =13.61 ±0.04A°
c =10.63 ±0.04A°.

The specific gravity as measured by flotation method using a mixture of benzene and 1-bromo naphthalene is 1.31, and with 4 molecules in the unit cell the mol wt calculates out to be 217.1, which corresponds reasonably with the reported molecular formula $C_{13}H_{14}ON_2$[1] within the limits of experimental observations.

The X-ray rotation and weissenberg photographs showed that the crystal is orthorhombic. Zero-layer. Weissenberg photographs of the crystal taken about *b* and *c* axes, and a higher layer photograph giving h k l reflections were used to determine the space group. There are no systematic absences in general h k l reflections; further the h k o, h o l and o k l reflections also show no systematic absences. The h o o, o k o, and o o l reflections are only present for h even, k even, and l even respectively. These suggest that the space group is $P2_12_12_1$.

A detailed comparative study of the single crystal data of harmidine and harmaline needs to be undertaken to explain the structural differences, if any, that exist between the two compounds.

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THE REACTION OF DIBROMOCARBENE WITH N-METHYLANILINE

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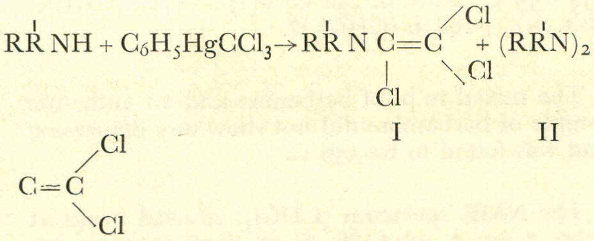
Previous studies of reaction of aliphatic secondary amines with dichlorocarbene (generated from chloroform and potassium *t*-butoxide) have been reported by Frankel *et al.*[1] Dialkylformamides were the major products isolated which are supposed to arise by hydrolysis of the intermediate amidodichlorides.

$$R_2NH + CCl_2 \rightarrow R_2NCHCl_2 \xrightarrow{H_2O} R_2NCHO$$

Parham and Potoski[2] have observed that the reactions of secondary amines with phenyl (trichloromethyl) mercury proceed in a different manner. Thus with *N*-methylaniline two compounds I and II were isolated.



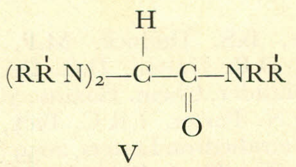
The author carried out the reaction of *N*-methylaniline with phenyl (tribromomethyl) mercury and isolated two compounds III and IV, the IV one being a new compound.

$RR'NCHO$ III $\quad (RR'N)_2C{=}C(NRR')_2$ IV

where $R{=}C_6H_5$

$R'{=}CH_3$

The reaction of *N*-methylaniline (25g) with phenyl (tribromomethyl) mercury (40g) in benzene solution was carried out at 80° for 2.5 hr in an inert atmosphere. Benzene was removed by distillation. The resulting mixture was treated with petroleum ether (b.p. 60–80c°) and filtered to remove phenylmercury bromide (90%). The filtrate was concentrated and chromatographed on neutral alumina. It was eluted with petroleum ether (b.p. 40–60c°), until no unreacted *N*-methylaniline was recovered. Further elution with 1:1 ether-benzene mixture gave slightly brown crystals of IV, yield 50% m.p. 118–19c° from ethanol; found, C, 80.4; H, 7.0; N, 12.5: $C_{30}H_{32}N_4$ requires: C, 80.4; H, 7.2; N, 12.5. Its structure was confirmed by IR spectrum and by hydrolysis to *N*-methylaniline (20%) and V (60%).



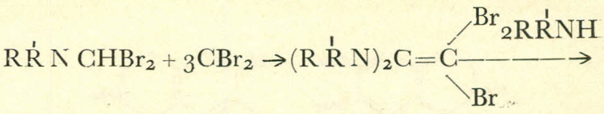
$$(RR'N)_2{-}\overset{\displaystyle H}{\overset{|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NRR'$$

V

The second fraction from the column was shown to be *N*-methylformanilide (III), yield 19% b.p. 128–29c°/15 mm. Its IR spectrum was identical to that of an authentic specimen.

The mechanism of this reaction seems to be in agreement with that of Parham *et al.*,[2] i.e. the initially formed dibromomethylaniline (VI) on the one hand is hydrolysed to *N*-methylformanilide (III) and on the other hand reacts with three equivalents of dibromocarbene to give VII. This in turn reacts with two moles of *N*-methylaniline to give the observed product (IV).

$$RR'NH + CBr_2 \text{—} \underset{VI}{RR'NCHBr_2} \xrightarrow{H_2O} \underset{III}{RR'NCHO}$$



VII

$$\underset{IV}{(RR'N)_2C{=}C(RR'N)_2}$$

It is a well known fact that gem-dibromo compounds are much more reactive than gem-dichloro compounds, which would account for the hydrolysis of VI and the formation of IV by nucleophillic displacement of Br.

Acknowledgement.—The author is grateful to Dr. E. J. Forbes for his guidance and to the Birmingham University for providing facilities to carry out this work.

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SPECTRAL STUDIES ON ALKALOIDS

Part III.*—The Identification of Berbenine as Berbamine

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Ikram and co-workers[1] have reported the isolation of three new alkaloids, named and for-

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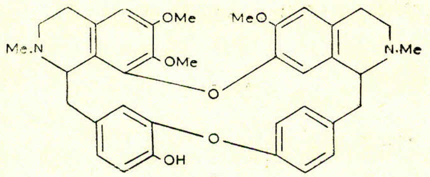
*Part I and II in this series are:

(I) The alkaloids of *Corydalis stewartii* Fedde: Corydinine, Pakistan J. Sci. Ind. Res., **11,** 337 (1968)

(II) The alkaloids of *Sarcococca saligna* Muell: Salignine, Pakistan J. Sci. Ind. Res., **12,**161 (1969) mulated as berbenine, $C_{19}H_{21}NO_3$, m.p. 152–153°C, berbericine, $C_{20}H_{17}NO_4$, m.p. 162–163°C and berbericinine iodide, C_{21} H_{22} NO_3 I, m.p. 205–206°C (dec) from the roots of *Berberis lycium* Royle. Umbellatine had already been isolated from it by Chatterjee.[2]

Berbenine was reported[1] to contain two methoxyl and one *N*-methyl group. It was inferred[1] from UV spectrum that berbenine might have an aporphine structure. The evidence presented in this paper indicates that berbenine is identical with berbamine(I).



I

The UV spectrum of berbenine in ethanol showed a maximum at λ_{max} 283 mμ (logε 3.91), indicating[3] a bisbenzyisoquinoline type structure for the alkaloid.

The mass spectrum of berbenine showed peaks at m/e 608, 593, 577, 395, 381, 364, 349, 198, 175 and 174. The molecular ion peak at m/e 608 suggested a molecular formula $C_{37}H_{40}N_2O_6$ for berbenine. The observed mass spectral fragmentation pattern is characteristic[4–6] of berbamine-oxycanthine type of alkaloids.

The NMR spectrum of berbenine in $CDCl_3$ showed peaks at 7.75, 7.45 (two N-CH_3 groups), 7.10 (ring-CH_2), 6.86, 6.40, 6.28τ(three O-CH_3) and signals for 10 protons in the aromatic region between 2.8 and 4.1τ.

The identity of berbenine with berbamine was established by means of mixed melting points and IR spectrum which were super-imposable.

In view of the above studies, it is confirmed that berbenine is identical with berbamine.

Experimental

The IR spectrum was taken in chloroform on a Beckmann IR-5 spectrophotometer. NMR spectrum, using tetramethylsilane as external standard, was taken in $CDCl_3$ solution on varian Associates A-60 high resolution NMR machine. The mass spectrum was measured on a AEI MS9 spectrometer.

Purification of Berbenine

Berbenine was repeatedly recrystallized from 95% ethyl alcohol giving colourless leaflets m.p. 154–155°C (lit. m.p. 156°C)7, $(\alpha)_D+111_c$°($CHCl_3$) (Lit. $(\alpha)_D+108.6$ ($CHCl_3$)7.

The mixed m.p. of berbenine and an authentic sample of berbamine did not show any depression and was found to be 156°C.

The NMR spectrum ($CDCl_3$) showed peaks at 7.75, 7.45, 7.10, 6.86, 6.40, 6.28, 4.03, 3.73, 3.5, 3.25 and 2.8τ.

The UV spectrum in ethyl alcohol showed λ_{max} 283 (log ε 3.91).

The mass spectrum showed peaks at m/e 608, 593, 5.77, 550, 501, 485, 417, 395, 381, 364, 349, 335, 323, 304, 198, 175 and 174. (Found: C, 72.01, H, 6.58; N, 4.76%. C_{37} H_{40} N206 requires: C, 72.91, H, 6.62, N, 4.60%).

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