# SHORT COMMUNICATIONS

## BUXPAPININE, A NEW ALKALOID FROM BUXUS PAPILOSA

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(Received June 15, 1968; revised August 28, 1968)

*Buxus papilosa* is available in Hazara and Rawalpindi District[1] and is used for various ailments. The alcoholic extract of the plant is fractionated into three fractions, i.e. weakly basic, moderately basic and strongly basic as described in previous communication.[2] Two new alkaloids buxpapine and buxpapamine[2] have been isolated from the strongly basic fraction. This paper describes the isolation and some of the properties of a third alkaloid, buxpapinine, m.p. 236–238°C, $C_{37}H_{52}N_2O_6$, obtained from weakly basic fraction by column chromatography.

The high resolution mass spectrum of buxpapinine showed a molecular ion peak at m/e 620 suggesting a molecular formula, $C_{37}H_{52}N_2O_6$ for it.

The IR spectrum of buxpapinine showed bands at 3450, 3030, 1735, 1670, 1610, 1590, 1520, 1490, 1310, 1240, 725 and 705 cm⁻¹. The bands at 3450 (N–H), 1670 (C=O), 1520 and 1310 cm⁻¹ suggested the presence of a secondary amide group, whereas those at 1735 and 1240 cm⁻¹ indicated the presence of an ester grouping. The bands at 3030, 1610, 1590, 1490, 725 and 705 cm⁻¹ might possibly be due to the presence of a phenyl ring in the molecule. The presence of an ester and amide grouping was also indicated by the UV absorption bands at 203 and 224 mμ.

The NMR spectrum ($CDCl_3$) showed peaks in the region 8.7–9.12τ (12H, multiplets, indicating the presence of at least four C-methyls), 7.72τ (6H, singlet, two N-Methyls), 7.85τ (3H, singlet) 7.97τ (3H, singlet) and complex peaks centered at 2.4τ (4–5 H, aromatic protons). The two methyl peaks at 7.85 and 7.97τ might be due to the presence of either CO–CH₃ or N–CH₃ groups.[3] No proton signal above 9.15τ was observed, indicating absence of cyclopropyl ring in the molecule. So far only one other non-cyclopropanoid alkaloid, buxeneine-G,[4] has been

isolated from *Buxus* species, out of more than 50 alkaloids having cyclopropane ring in the 9–10 position.[5]

Chemical studies are in progress to determine the nature of the amide and ester groupings and the basic skeleton of buxpapinine.

Another alkaloid, m.p. 310°C(dec) has also been obtained from fractions eluted by ethyl acetate–ethyl alcohol, mixture. Studies are in progress on its purification and identification.

### Experimental

All m.ps are uncorrected. UV spectrum was measured in 95% ethanol using a Perkin Elmer UV-Visible spectrophotometer, Model 202. The IR spectrum was taken in KBr pellet on Perkin Elmer IR-spectrophotometer, model 237. The NMR spectrum was taken in $CDCl_3$ on a Varian Associate Model A-60 high resolution N.M.R. spectrometer. The mass spectrum was taken on a MS 9 high resolution mass spectrometer.

*Chromatography of Weakly Basic Fraction.*—5 kg dried leaves and stems of *Buxus papilosa* gave, after usual work-up,[2] 2.08 g weak bases. The weak bases (20.0 g) were dissolved in benzene, charcoaled, dried ($Na_2SO_4$) and chromatographed on a column of alumina (350.0 g, M&B. Ltd.) prepared in benzene. The column was eluted with pure benzene, benzene–ethyl acetate (4:1), benzene–ethyl acetate (1:1), pure ethyl acetate, ethyl acetate–ethyl alcohol (1:1) and finally dry ethyl alcohol. The following fractions of 400 ml each were collected: fraction I–IV with benzene; V with benzene–ethyl acetate (4:1); VI with benzene–ethyl acetate (1:1); VII–IX with pure ethyl acetate, X–XI with ethyl acetate–ethyl alcohol (1:1) and fraction XII with pure ethyl alcohol.

*Fraction IX (Provisionally Named as Buxpapinine).*—The solvent was removed under reduced pressure. The residue recrystallized from acetone to give 0.5 g of a substance, m.p. 236–238°C. Recrystallization from absolute ethyl alcohol yielded colourless shining needles, m.p. 253–255°C, $[\alpha]_{25}^{D}$ −53° (c=1.24, $CHCl_3$). The IR spectrum (KBr) showed bands at 3450, 3030, 2980, 2950, 2830, 1735, 1670, 1610, 1590, 1520, 1490, 1370, 1310, 1240, 1025, 725 and 705 cm⁻¹. The NMR

spectrum (CDCl$_3$) showed peaks at 8.7–9.12, 7.72, 7.85, 7.97, and 2.4τ. UV bands at 203 and 224 mμ. (Found: C, 70.56; H, 8.79 and N, 4.06%. C$_{37}$H$_{52}$N$_2$O$_6$ requires: C, 71.5; H, 8.4; N, 4.15%.)

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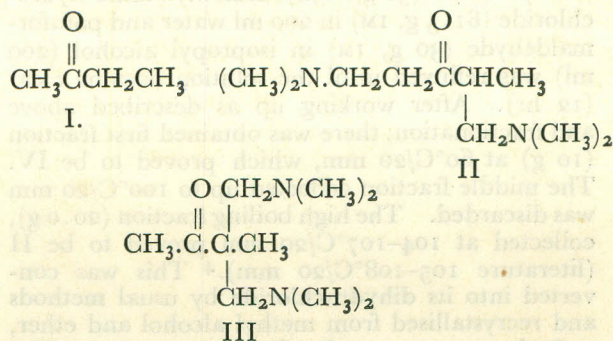
## ORIENTATION IN THE MANNICH REACTION

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The structure of the Mannich base, monoamine or diamine, formed from an unsymmetrical ketone, such as compound I, has always been in dispute. Thus, diamine obtained from ethyl methyl ketone (I) has been stated to be either 1-dimethylamino-4-dimethylamino-methyl-3-pentanone (II) or 3,3-bis(dimethylaminomethyl)-2-butanone (III) by Cardwell,[1] but according to Haeussler and Schacht[2] the diamine has structure III. Barrett and Chambers[3] and Blicke and McCarty[4] favour structure II for it. We have now employed NMR spectroscopy to establish the structure of the diamine obtained from 1 mole of ethyl methyl

*Taken in part from the M.Sc. thesis of A.K.B. submitted to Department of Chemistry, University of Peshawar, in July 1968.

ketone, 2 moles of formaldehyde and 2 moles of dimethylamine hydrochloride.

$$\underset{\text{I.}}{CH_3CCH_2CH_3} \qquad \underset{\underset{\displaystyle CH_2N(CH_3)_2}{|}}{(CH_3)_2N.CH_2CH_2CCHCH_3}$$
$$\text{II}$$

$$\underset{\underset{\displaystyle CH_2N(CH_3)_2}{|}}{\overset{\overset{\displaystyle O}{\|}\ \ \overset{\displaystyle CH_2N(CH_3)_2}{|}}{CH_3.C.C.CH_3}}$$
$$\text{III}$$

The NMR spectrum of the purified diamine showed peaks at 9.02 (3H, doublet, $J$=4.0 c/s, CH—CH$_3$), 7.85 (12H, singlet, four N—CH$_3$), 7.43 (4H, multiplet, two N—CH$_2$) and 6.37τ (2H, —COCH$_2$-). The presence of 3 methylenes and the fact that C-methyl at 9.02τ is a doublet and not a singlet definitely favour structure II for it.

The NMR spectrum of the purified Mannich base (monoamine) from I showed peaks at 9.01 (3H, doublet, —CH-CH$_3$), 7.91 (singlet, COCH$_3$) 7.84 (6H, singlet, two N—CH$_3$), 7.55 (2H, doublet, unclean, N-CH$_2$) and 4.31τ (1H, multiplet). The presence of a singlet methyl peak at 7.91τ and a doublet at 9.01τ definitely establish its structure as IV, as is generally believed.[5,6]

$$\underset{\underset{\displaystyle CH_2N(CH_3)_2}{|}}{\overset{\overset{\displaystyle O}{\|}}{CH_3CCHCH_3}}$$
$$\text{IV}$$
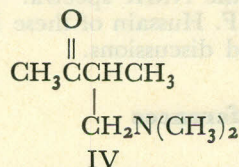
It may be interesting to mention here that while the product IV is the expected one,[7] resulting from the acid-catalyzed enolization of ethyl methyl ketone (I), the formation of II cannot be explained on this basis. Studies are in progress to clarify these apparent anamolies regarding mechanism of the Mannich reaction.

### Experimental

*Preparation of 3-dimethylaminomethyl-2-butanone (IV).*—A mixture of ethyl methyl ketone (7.2 g, 0.1 M), dimethylamine hydrochloride (4.1 g, 0.05M) and paraformaldehyde (2.4 g, 0.08 M) in 50 ml isopropyl alcohol was refluxed until the solution became clear (6–8 hr). After usual work-up,[4] the Mannich base IV was collected at 60°C/18–20 mm (literature 58°C/15 mm)[4]; yield 5.0 g (75%). The NMR spectrum [(CD$_3$)$_2$SO$_4$] showed peaks at 9.01, 7.91, 7.84, 7.55 and 4.31τ.

*Preparation of 1-dimethylamino-4-dimethylaminome-thyl-3-pentanone ( II ).*—(i) A mixture of ethyl methyl ketone (36 g, 0.5M), dimethylamine hydrochloride (81.5 g, 1M) in 200 ml water and paraformaldehyde (30 g, 1M) in isopropyl alcohol (200 ml) was refluxed until the solution became clear (12 hr). After working up as described above and fractionation, there was obtained first fraction (10 g) at 60°C/20 mm, which proved to be IV. The middle fraction collected up to 100°C/20 mm was discarded. The high boiling fraction (20.0 g), collected at 104–107°C/20 mm proved to be II (literature 105–108°C/20 mm).[4] This was converted into its dihydrochloride by usual methods and recrystallised from methyl alcohol and ether, melted at 191–193°C (literature 192–93°C).[4] The NMR [ $(CD_3)_2SO_4$.] spectrum of II showed peaks at 9.02, 7.85, 7.43 and 6.37τ.

(ii) Compound II was also prepared using 1 mole of IV, 1 mole of dimethylamine hydrochloride and 1 mole of paraformaldehyde in 200 ml ethyl alcohol. After usual work-up and fractionation, 50 g of II were collected at 104–107°C/20 mm.

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# A STUDY OF THE PHASE COMPOSITION OF ZIARAT LATERITES

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Fifteen million tons of laterite deposits have been reported from Ziarat area. This estimate is based on about quarter of the laterite-bearing area. It has 29, 30 and 5% average contents of iron, alumina and titanium oxide, respectively.[1] Thirty samples provided by Geological Survey of Pakistan, Quetta, have been analysed in these Laboratories and have shown variations in contents in the range 20–42% iron, 16–43% alumina, 2–6.5% titanium oxide and 3–20% silica.[2] It has been shown that alumina of high purity suitable for aluminium metal industry could be manufactured from grades having not more than 5% silica. The residues after the extraction of alumina become rich in iron content and possible use as iron ore has been suggested. The residues have been analysed for their chemical composition and their use has been worked out as hydrogen sulphide absorbent in water gas purification.[3] No attempt has been made so far to assess and evaluate ziarat laterites as a source of iron for steel industry. The deposit being low-grade could possibly be economically processed for the production of iron or steel, if the other major constituents, i.e. alumina and titania, are also separated and utilized.

A simple floatation technique was used to investigate the possibility of enrichment of the ore by removing silica from it. The floatation process showed little variation of silica percentage in the final concentrate. At this stage it was thought worthwhile to investigate the phase composition of laterites which may provide effective means for exploitation of this ore.

## Experimental and Results

*Determination of Ferrous Iron.*—Ferrous iron was determined by a standard method in slightly modified form.[4] Final titrations were done against potassium permangnate. Experiments carried out with 0.1 g of metallic iron powder showed a maximum of 6% error. Further standardization was also carried out by mixing the iron powder with completely oxidized ore. The results

TABLE I.—PHASE ANALYSIS BY CHEMICAL METHODS.

| Sample No. | 3 | 5 | 9 | 10 | 14 | 15 | 16 | 19 | C | E |
|---|---|---|---|---|---|---|---|---|---|---|
| Colour | Red | Red | Red | Red | Yellowish brown | Yellowish brown | Straw brown | Light yellow | Red | Red |
| Ferrous iron wt % as FeO | 0.2+0.012 | 0.1+0.01 | 0.2+0.012 | 0.2+0.012 | 1.64+0.098 | 0.44+0.026 | 5.76+0.345 | 3.57+0.214 | 0.36+0.022 | 0.49+0.029 |
| Free silica wt % | Trace | Trace | — | 0.16+0.018 | — | 0.24+0.026 | 0.32+0.035 | — | 0.27+0.03 | — |
| Acid insolubles wt % | 49.9 | 56.0 | 55.5 | 56.7 | 55.4 | 46.3 | 51.9 | 62.9 | 46.9 | 42 |
| Free water wt % | 1.49 | 0.86 | 1.04 | 1.4 | 1.25 | 2.11 | 1.42 | 1.22 | 0.79 | — |
| Hematite ($Fe_2O_3$) wt% | 39.38 | 47.64 | 41.67 | 44.92 | 27.78 | 41.12 | 32.72 | 24.05 | 52.40 | 48.06 |
| Aluminium silicates (clays) maximum wt% | 8.80 | 21.83 | 8.80 | 27.34 | 6.66 | 36.77 | 22.57 | 22.71 | 23.01 | 4.16 |
| Free Alumina maximum wt% | 30.86 | 14.87 | 34.52 | 15.06 | 40.98 | nil | 22.68 | 29.80 | 5.58 | 24.27 |
| Chamosite maximum wt % | 0.5 | nil | nil | nil | nil | 1.0 | 4.0 | 2.1 | 0.84 | nil |
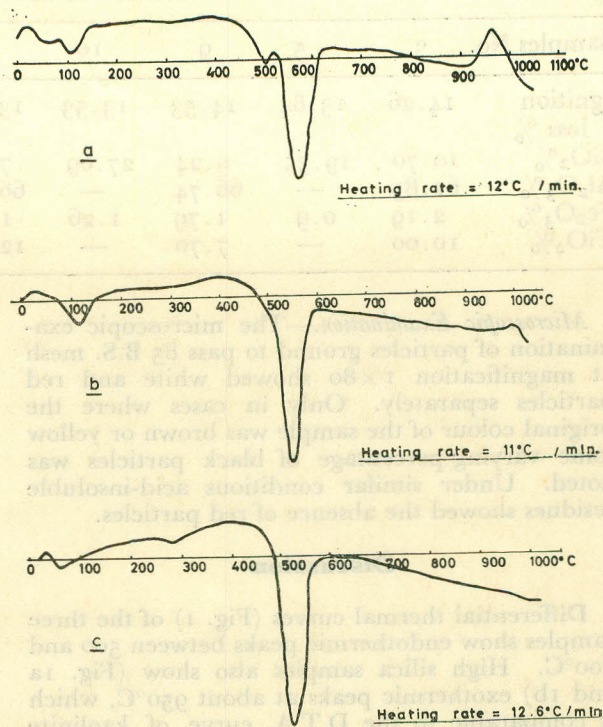
Fig. 1.—Differential thermal analysis curves of acid insolubles (a) sample No. C. (b) sample No. 15 (C) sample No. 14.

have been shown with possible maximum error (Table 1).

*Determination of Acid Insolubles.*—15.0 g sample and 50 ml concd HCl were heated over water bath for ½ hr and the product allowed to stand for another ½ hr. The residue was washed thrice by decantation with 200 ml tap water in each case, allowing the settling time from 2 hr to overnight. The residue was then dried at 110°C, was white to light grey. The acid-soluble mass was found to contain only iron, except in few cases where calcium and magnesium salts were present.

*Determination of Free Silica.*—Hilbrand *et al.*'s method[5] was further standardized by using very finely ground pure quartz as standard. Free silica contents were determined in acid insolubles and then calculated on the basis of original ore. It was possible to calculate maximum limit of errors (Table 1).

*Differential Thermal Analysis.*—The differential thermal analysis (D.T.A) was performed on some of the acid insolubles with an apparatus assembled and standardized in these Laboratories.[6]

TABLE 2.—ANALYSIS OF ACID INSOLUBLES.

| Samples No. | 3 | 5 | 9 | 10 | 14 | 15 | 16 | 19 | C | E |
|---|---|---|---|---|---|---|---|---|---|---|
| Ignition loss % | 14.26 | 13.84 | 14.53 | 13.53 | 13.53 | 15.72 | 16.25 | 19.97 | 14.43 | 14.66 |
| $SiO_2$% | 10.70 | 19.35 | 9.24 | 27.69 | 7.09 | 21.75 | — | 15.98 | 25.40 | 6.47 |
| $Al_2O_3$% | 62.85 | — | 66.74 | — | 66.36 | — | — | 53.43 | 53.18 | 69.08 |
| $Fe_2O_3$% | 2.19 | 0.9 | 1.79 | 1.26 | 1.00 | 0.60 | 1.59 | 1.39 | 1.00 | 1.79 |
| $TiO_2$% | 10.00 | — | 7.70 | — | 12.00 | — | 5.00 | 9.23 | 5.99 | 8.00 |

*Microscopic Examination.*—The microscopic examination of particles ground to pass 85 B.S. mesh at magnification $1 \times 80$ showed white and red particles separately. Only in cases where the original colour of the sample was brown or yellow some varying percentage of black particles was noted. Under similar conditions acid-insoluble residues showed the absence of red particles.

## Discussion

Differential thermal curves (Fig. 1) of the three samples show endothermic peaks between 500 and 600°C. High silica samples also show (Fig. 1a and 1b) exothermic peaks at about 950°C, which is comparable to the D.T.A. curve of kaolinite clays. The exothermic peak between 900 to 1000°C is missing in low silica samples Fig. 1c. This suggests that hydrated alumina (diaspore or boehmite) may be present. Free silica is almost absent in all the tested samples (Table 1). Ferrous iron is almost negligible in red samples (Table 1) and is significant in light brown or yellow samples. Only few samples were of other colours than red. The average ferrous iron contents in the samples which were expected to be high in ferrous iron was 1.27%. It is also interesting to note that titanium percentage is considerably increased in acid insolubles (Table 2). This shows that titanium is not associated with iron as mineral.

In view of the foregoing results the following conclusions can be drawn: Nearly all the iron present in Ziarat Laterites is as $Fe_2O_3$ (hematite). All of the silica is in the form of silicates, mainly as aluminium silicate. Alumina in the high alumina samples is also present as free alumina and a part of it in the hydrated form which could not be estimated. Titanium may be present as $TiO_2$.

Apart from these main phases, small percentage of ferrous iron, calcium or magnesium carbonates are also present. Dbir *et al.*[7] have reported only a brief qualitative account and the present results are in general agreement, but differ in reporting chamosite not to any significant amount. MgO varies from 0 to 2% and it indicates that all the ferrous iron is not present as chamosite. Chamosite calculated from quantitative analysis does not exceed 4% in any sample. This estimate is based on the assumption as if all the magnesium is present as a part of chamosite not as $MgCO_3$.

Iron being present as $Fe_2O_3$ might be quantatively reduced to $Fe_3O_4$ or Fe without fusing the mass with carbon by one of the methods,[8-10] used for similar type of ores.

Preparation of high grade alumina and $TiO_2$ or other commercial scale products from this ore before or after the recovery of iron, may place it at higher economic position than Kalabagh iron ores.

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# BOOK NOTICES

*Book Reviews*

**Chymia, Vol. 12. Annual Studies in the History of Chemistry.**—H.M. Leicester, Editor-in-Chief. University Pennsylvania Press. Price $8.50.

A reviewer is expected to introduce a publication appreciating its contents but more so knowing the intellectual requirements of the average reader of the journal to whom the review is being presented. Culture, as distinct from science, is not popular in Pakistan, due probably to its being a relatively young state. However natural inquisitiveness which draws one to science also takes one further to know, how that particular science arose, asking, who were its makers. Thus many would be surprized to know that Newton, besides being the greatest mathematician and physicist of his age, was also an alchemist. This should whet one's appetite to read for "the first time a complete alchemical manuscript transcribed by Sir Isac Newton". Most readers of this journal are Muslims whom articles on Arabic minting of gold and silver coins as also on Arabic Minerology of the tenth century should make an immediate appeal. When Kekule′ formulated his theory of Benzene Ring organic chemistry began to develop by leaps and bounds. Alfred Werner, who got Nobel Prize, can be spoken of as the Kekule[I] of Inorganic Chemistry. And there are four articles on him. There is an inspring sketch of the Bulgarian chemist, Prop. Raikov of whom it can be said that, "many generations of excellent chemists had attended his school and gone on to work in the newly developing industry of the (then) recently liberated Bulgarian State". In India Sir P.C. Ray was the "Guru" of almost all the famous chemists of Bengal as he was also the founder of the Bengal Chemical and Pharmaceutical Works, Calcutta. Raikov was the Ray of Bulgaria and his life sketch can inspire any senior chemist of Pakistan, which is today what Bulgaria was about 1880. The Swedish chemist, Bergman, is one of the founders of modern chemistry. "There is no comprehensive biography of Bergman in English", hence the justification of a long article devoted to him. There is a sensational

account of how the French chemist, Rezoir, exploited the property of hydrogen, filled a baloon to cross the English Channel, but died in the accident as the first aeronaut. There are four more articles: one on Davy, second on the Law of Dulong and Petit, third on Avogadro's ideas of molecules, and a fourth on the history of chemistry in Argentine of 1800 A.D. The publication is priced $8.50 which is not beyond the budget of most colleges in Pakistan.

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**Physical Chemistry.**—Third edition. Walter J. Moore. 844 pp. Prentice-Hall, Inc., Englewood Cliffs, N.J., U.S.A.

In this edition many improvements in presentation have been made by the author in every chapter. Chemical kinetics and electrochemistry have been treated in the earlier portion of this edition in order to familiarise the reader in the beginning with two major branches of physical chemistry. According to the need of the time a few more chapters such as High Polymers and Radioactivity have been added. Recent advances in nuclear, atomic, and molecular structure have been described. One of the special features of this edition is that it deals with the problems of physical chemistry without involving much higher mathematics. Chapters II, III and VI deal with thermodynamics while in chapter XIX the author has described chemistry of high polymers with special reference to their molecular weight determination by various physicochemical methods. The idea of wave mechanics is represented very nicely in chapter XII. Electrochemistry has been divided into two chapters and in the chapter dealing with the chemical bond approach, molecular orbitals of benzene and hydrogen bonding have been treated in the most modern way.

This book not only covers the B.Sc. physical chemistry syllabus for all Pakistani universities but is also very useful for M.Sc. students.