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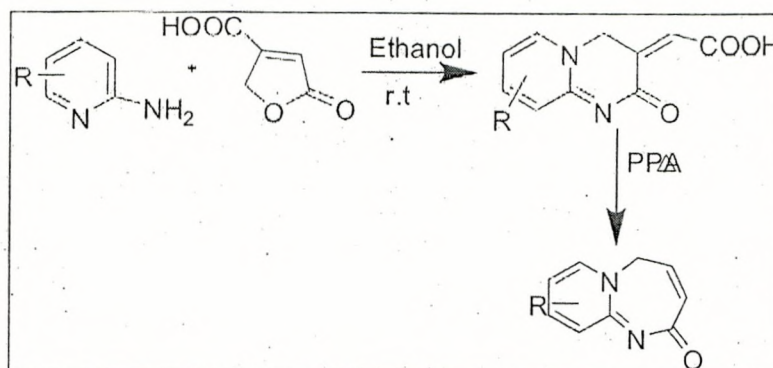
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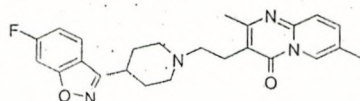


A highly efficient one-pot simple synthesis of 2-[2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid is described. The rearrangement of 2-[2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid in the presence of polyphosphoric acid (PPA) yielded a seven-membered diazepine with decarboxylation and ring expansion.

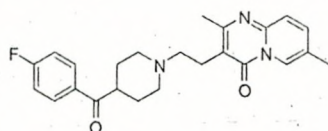
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INTRODUCTION

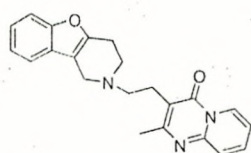
Pyrido[1,2-a]pyrimidines have aroused much interest from medicinal chemists as a result of their valuable biological properties [1–5]. The pyrido[1,2-a]pyrimidine core is present in drugs including risperidone, an antipsychotic agent, metreperone, a selective 5HT₂ receptor antagonist, and lusaperidone, an antidepressant [6–8].



1a Risperidone



1b Metreperone



1c Lusaperidone

The development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic synthesis. Generally, the pyridopyrimidine ring is constructed by condensation based on the amidine fragment of 2-aminopyridine or its derivatives with various acylating and alkylating agents [9–15]. In this communication, we report an environmentally benign synthesis of pyrido[1,2-a]pyrimidine-2-ones and its thermal rearrangement into diazepines in the presence of polyphosphoric acid.

Aconic acid, a five-membered synthon, was used as starting material for the synthesis of quinoline acetic acids that were versatile precursor for the synthesis of furo, thieno and pyrrolo(2,3-b) quinolines [16–19]. In a similar way, we tried to construct pyridopyrimidine acetic acids from 2-amino pyridine and aconic acid. Generally, acids require *N,N'*-dicyclohexylcarbodiimide (DCC) for activation. However, in our case, aconic acid itself reacted with 2-amino pyridine without any such activation with catalyst, which made the reaction versatile.

RESULTS AND DISCUSSION

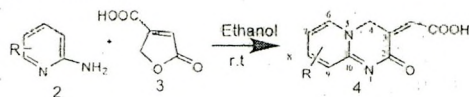
Initially, the thought was to prepare the pyridopyrimidine acetic acid in two steps viz (i) preparation of aconyl chloride and subsequent preparation of the *N*-(α -pyridyl)aconamide (ii) and cyclization of aconamide to pyridopyrimidine acetic acid (Scheme 1).

However, synthesis of pyridopyrimidine acetic acid from aconic acid and 2-amino pyridine was not feasible as we

Scheme 1. Preparation of aconamide.



Scheme 2. Synthesis of (Z)-2-(2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene)acetic acid.



Entry (R)	Reactant	Product
a	H	H
b	3Me	9Me
c	4Me	8Me
d	5Me	7Me
e	6Me	6Me
f	4,6 Dimethyl	8,6 Dimethyl
i	5Br	7Br
j	3Me,5Br	9Me,7Br
h	4Me,5Br	8Me,7Br

failed to arrive at the intermediate aconamide. Hence, an alternative reaction of 2-amino pyridine with acryloyl acid was carried out in alcohol at room temperature. The reaction proceeded smoothly with the formation of desired pyridopyrimidine acetic acid in good yields (Scheme 2).

The structures of the products (4a-h) were confirmed by IR, ^1H ^{13}C NMR spectroscopy and mass spectrometry. The mass spectrum of (4a) displayed the molecular ion (M^+) peak at m/z 204 that is consistent with the proposed structure. The IR spectrum displayed a broad band at 2923 cm^{-1} along with a strong $\text{C}=\text{O}$ band at 1714 cm^{-1} that indicated the presence of carboxylic acid group in the structure. Another strong $\text{C}=\text{O}$ resonance at 1670 cm^{-1} was attributed to the $\text{C}=\text{O}$ group at second position. Analysis of the NMR spectrum of the compound 4a revealed six signals for protons at δ 5.00, 6.3, 6.8, 6.9, 7.7, 7.8 and ten signals for carbon at δ 73, 112, 113, 122, 134, 144, 153, 164, 167, 177. DEPT-135 spectrum showed the presence of five methine carbons and one methylene carbon. Hence, the remaining four carbons must be quaternary that was in accordance with the proposed structure.

The signal at δ 7.8 was assigned to $\text{C}_6\text{-H}$ because it is deshielded by the neighboring nitrogen. C_7 proton and C_9 proton appeared at δ 6.8 and 6.9 as triplet and doublet respectively because they experience shielding effect by virtue of the position and nature of bonding [20]. The signal for proton at C_8 appeared as doublet at δ 7.7. The protons resonating at δ 6.3 and δ 5.0 were because of $\text{C}_3\text{-H}$ and $\text{C}_4\text{-H}$.

The ^{13}C signals were assigned using HETCOR. The signals of carbon at δ 73, 112, 113, 122, 134 and 144

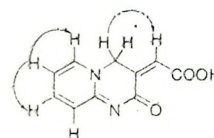


Figure 1. COSY correlations observed in 2-[2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid.

correlated with the proton signals at δ 5.00, 6.3, 6.8, 6.9, 7.7 and 7.8 respectively. The positions of the quaternary carbons were assigned using HMBC spectrum. The signals at δ 164 and 167 showed correlation with the exocyclic methine proton. Hence, δ 167 was assigned to the carboxyl carbon and the signal at δ 164 to C_{10} .

As expected, a strongly deshielded aromatic proton at the C_6 position as a result of the anisotropy of the carbonyl group at the C_4 position [21,22] was not observed in the ^1H NMR spectrum which indicated that the product formed was the 2-oxo isomer and not the 4-oxo isomer. The regiochemistry of the structure was also determined by 2D NMR studies. A long range $^3\text{J}_{\text{CH}}$ correlation between H_6 and C_4 is expected of a 4-oxo isomer. Instead of such correlation, a $^3\text{J}_{\text{CH}}$ correlation between the carbon resonating at δ 122 ppm and δ 72 ppm was noticed confirming the suggested structure 2-oxo isomer. The COSY and HMBC correlations are given in Figures 1 and 2.

A mechanistic rationalization of the product formed is given in Scheme 3, which involves the initial condensation of amino group of pyridine nucleus with acid and cyclization by the nucleophilic attack of ring nitrogen to the carbon attached to the oxygen at ring junction (Scheme 3). Of the 12 entries, no reaction was observed between 5-nitro-2-aminopyridine and 3-methyl-5-nitro-2-aminopyridine even under reflux. This may be because of the strong electron withdrawing effect of nitro group that decreases the release of electron from the ring nitrogen. Usually, in the case of 6-substituted-2-aminopyridines, condensation with participation of the ring nitrogen atom does not occur because of steric hindrance [23]. However, in this case, no such steric hindrance was found to play a role and the reaction went smoothly with the 6-methyl-2-aminopyridine also.

Unsaturated bicyclic and polycyclic nitrogen bridge head ring systems containing a carbonyl group and substituent in the peri positions undergo ring transformation under heating in high boiling solvents and Dowtherm A [24-26] to give condensed ring systems (Scheme 4).

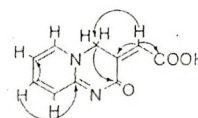
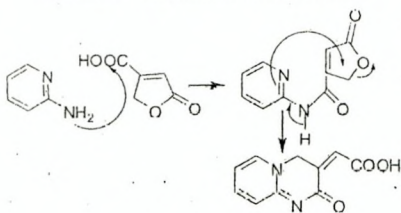


Figure 2. HMBC correlations observed in 2-[2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid.

Scheme 3. Mechanism of the reaction.



Scheme 4. Ring transformation of pyrido[1,2-a]pyrimidine to 1,8-naphthyridine.



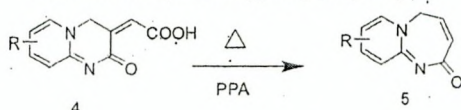
This type of ring transformation is involved in the synthesis of nalidixic acid and related antibacterial agents starting from α -azaamino methyl malonates [27].

Hence, an attempt was made to transform 2-oxo-2H-pyrido[1,2-a]pyrimidin-ylidene acetic acid into 1,8-naphthyridine derivatives. For this purpose, 2-oxo-2H-pyrido[1,2-a]pyrimidin-ylidene acetic acid was refluxed with polyphosphoric acid in a steam bath. Contrary to our expectation, the reaction underwent a thermal rearrangement yielding pyridodiazepines (Scheme 5).

The $^1\text{H-NMR}$ spectrum exhibited signals at δ 4.5, 6.2, 6.9, 7.2, 7.6, 8.2, 8.4, and ^{13}C spectrum displayed nine signals at δ 52, 113, 119, 128, 137, 144, 147, 151 and 170 instead of ten signals expected, along with M^+ peak at m/z 160 in the mass spectrum. These two facts clearly indicated that decarboxylation could have occurred during the reaction.

A comparison of $^1\text{H-NMR}$ spectrum of the product with that of the 2-oxo-2H-pyrido[1,2-a]pyrimidin-ylidene acetic acid showed the presence of only two quaternary carbon atoms in the product instead of four. Also, the number of methine carbon had increased from five to six. Hence, it was concluded that among the four quaternary carbons present in the reactant, one carbon had left as CO_2 and the carbon at δ 164 must have been protonated. This has also been confirmed by the shift in the ^{13}C resonance of the sp^3 -hybridized carbon atom from δ 73 to δ 52 (a shift

Scheme 5. Formation of pyrido[1,2-a]diazepine.



Entry (R)	Reactant	Product
a	H	H
b	6Me	6Me
c	5Me	7Me

of 21 ppm) in the product as a result of the alpha effect observed with sp^3 -hybridized carbon atoms attached to the $=\text{CH}$ in α position. Therefore, it was concluded that a methine group had been attached to the methylene carbon resonating at δ 73 in the reactant 4. Further, the $^1\text{H-NMR}$ spectrum exhibited a very characteristic splitting pattern, that is, a doublet of triplet at δ 6.2 integrating for one proton indicating the presence of the $\text{CH}_2\text{-CH}=\text{CH}-$ moiety. Hence, it was concluded that a ring expansion could have occurred with the formation of a seven-membered ring with the pyrido nucleus, which was identified as pyrido[1,2-a][1,3]diazepin-2(5H)-one. The structure of the compound was also confirmed from 2D spectra. Possible mechanism for the formation of pyrido[1,2-a][1,3]diazepin-2(5H)-one is given in Scheme 6. The reaction is supposed to take place by decarboxylation followed by a rearrangement giving a three-membered ring, which subsequently opens to give a ring-expanded product.

EXPERIMENTAL

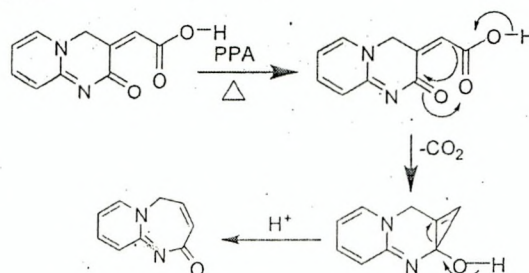
General. Melting points were determined using Biochem melting point apparatus and are uncorrected. The IR spectra were recorded in KBr pellet technique on a PerkinElmer spectrophotometer. Absorption frequencies are quoted in reciprocal centimeter.

$^1\text{H-NMR}$ spectra were determined by Bruker Avance 500 MHz instrument in D_2O , CDCl_3 , with tetramethylsilane as internal reference. Chemical shifts are quoted in parts per million (ppm) (s = singlet; d = doublet; t = triplet and m = multiplet).

Mass experiments were performed on GC (T 8000 TOP CE) and combined with mass spectrometer (Md 800 FIS ONS). Thin layer chromatography was performed using glass plates coated with silica gel G to monitor and check the completion of each reaction. Petroleum ether (60–80), ethyl acetate and ethyl alcohol were used as the developing solvents. Spots were detected with UV light and iodine. Aconic acid was prepared using the literature method [26].

General procedure 4. To a magnetically stirred solution of aconic acid (0.02 mole) in alcohol added drop wise the alcoholic solution of 2-amino pyridine (0.01 mole) at room temperature. The precipitated solid was filtered, dried and was recrystallised from ethanol as colorless crystals.

Scheme 6. Mechanism for the formation of pyrido[1,2-a][1,3]diazepin-2(5H)-one.



2-[2-Oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4a). 4 g (91%) mp 221°C IR (ν_{max}): 2954 cm^{-1} (–OH), 1741 cm^{-1} (–CO), 1670 cm^{-1} (–CO), 1637 cm^{-1} (–CN), 1271, 985 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.3 (d, $J=2$ Hz, 1H, CH), 5.00 (s, 2H, CH_2), 7.8 (t, $J=8$ Hz, 1H, CH), 6.8 (t, $J=6.5$ Hz, 1H, CH) 7.7 (d, $J=6.5$ Hz, 1H, CH) 6.9 (d, $J=8$ Hz, 1H, CH) ^{13}C NMR (125 MHz, D_2O) 177, 164, 122, 167, 73, 144, 112, 134, 113, 153. GCMS (IE, m/z): 204 (21), 193 (8), 186 (11), 180 (20), 159 (4%), 146 (17), 118 (22), 95 (0), $m/z=88$ (45%), (20), 66 (34) Anal. For $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_3$ Calcd. C, 58.82; H, 3.95; N, 13.72%. Found: C, 58.7; H, 3.81; N, 13.7%.

2-[9-Methyl-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4b). 4.56 g (96%) mp 232°C, IR (ν_{max}): 3010 cm^{-1} (–OH), 1748 cm^{-1} (–CO), 1666 cm^{-1} (–CO), 1640 cm^{-1} (–CN), 1269, 983 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.3 (t, $J=2$ Hz, 1H, CH), 5.00 (s, 2H, CH_2), 7.7 (dd, $J=7.5$ Hz, 1H, CH), 6.8 (t, $J=7$ Hz, 1H, CH) 7.6 (dd, $J=7$ Hz, 1H, CH) 2.10 (s, 3H, CH_3) ^{13}C NMR (125 MHz, D_2O) 177, 143, 122, 164, 73, 132, 105, 113, 120, 15, 152. GCMS (IE, m/z): 218 (80), 207 (2), 189 (2), 106 (100), 96 (33), 78 (55), 69 (2), 55.5 (4). Anal. For $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_3$ Calcd. C, 60.55; H, 4.62; N, 12.84%. Found: C, 60.48; H, 4.60; N, 12.7%.

2-[8-Methyl-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4c). 4.4 g (93%) mp 233°C, IR (ν_{max}): 3014 cm^{-1} (–OH), 1749 cm^{-1} (–CO), 1668 cm^{-1} (–CO), 1640 cm^{-1} (–CN), 1269, 983 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.3 (t, $J=4$ Hz, 1H, CH), 4.9 (s, 2H, CH_2), 7.7 (d, $J=8$ Hz, 1H, CH), 6.7 (dd, $J=8$ Hz, 1H, CH), 6.8 (s, 1H, CH), 2.2 (s, 3H, CH_3) ^{13}C NMR (125 MHz, D_2O) 173, 162, 121, 164, 71, 151, 109, 141, 20, 113, 157. GCMS (IE, m/z): 218 (60), 207 (88), 191 (9), 165 (9), 129 (21), 119 (32), 106 (60), 91 (61), 60 (100), 57 (63), 5 (28) Anal. For $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_3$ Calcd. C, 60.55; H, 4.62; N, 12.84%. Found: C, 60.40; H, 4.60; N, 12.8%.

2-[7-Methyl-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4d). 4.1 g (88%) mp 233°C, IR (ν_{max}): 3012 cm^{-1} (–OH), 1752 cm^{-1} (–CO), 1671 cm^{-1} (–CO), 1642 cm^{-1} (–CN), 1271, 980 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.47 (t, $J=2$ Hz, 1H, CH), 5.00 (s, 2H, CH_2), 7.6 (dd, $J=2$ Hz, 1H, CH), 6.8 (d, $J=9$ Hz, 1H, CH) 7.4 (t, $J=8$ Hz, 1H, CH), 2.10 (s, 3H, CH_3) ^{13}C NMR (125 MHz, D_2O) 176, 161, 122, 165, 72, 146, 123, 16, 132, 113, 152. GCMS (IE, m/z): 218 (60), 204 (8), 192 (3), 186 (8), 168 (87), 161 (9), 154 (7), 154 (5), 146 (7), 136 (9), 125 (24), 118 (6), 105 (100), 96 (80), 88 (33), 77 (42), 70 (30) Anal. For $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_3$ Calcd. C, 60.55; H, 4.62; N, 12.84%. Found: C, 60.50; H, 4.57; N, 12.8%.

2-[6-Methyl-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4e). 3.88 g (82%) mp 234°C, IR (ν_{max}): 2995 cm^{-1} (–OH), 1748 cm^{-1} (–CO), 1668 cm^{-1} (–CO), 1640 cm^{-1} (–CN), 1270, 981 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.47 (t, $J=4$ Hz, 1H, CH), 5.0 (s, 2H, CH_2), 6.6 (d, $J=4$ Hz, 2H, CH), 7.5 (q, $J=4$ Hz, 1H, CH), 2.3 (s, 3H, CH_3) ^{13}C NMR (125 MHz, D_2O) 175, 162, 123, 165, 73, 148, 19, 111, 112, 145, 156. GCMS (IE, m/z): 218 (60), 207 (2), 189 (2), 106 (100), 96 (33), 78 (55), 69 (2), 55.5 (4) Anal. For $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_3$ Calcd. C, 60.55; H, 4.62; N, 12.84%. Found: C, 60.40; H, 4.60; N, 12.7%.

2-[6,8-Dimethyl-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4f). 4.26 g (85%) mp 242°C, IR (ν_{max}): 2995 cm^{-1} (–OH), 1748 cm^{-1} (–CO), 1668 cm^{-1} (–CO), 1640 cm^{-1} (–CN), 1270, 981 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.3 (t, $J=4$ Hz, 1H, CH), 5.0 (d, $J=2$ Hz, 2H, CH_2), 6.6 (s, 2H, CH), 2.3 (s, 3H, CH_3) ^{13}C NMR (125 MHz, D_2O) 177, 152, 163, 73, 145, 23, 110 (2C), 19, 121, 157. GCMS (IE, m/z): 234 (51), 197 (100),

195 (99), 170 (19), 173 (18), 126 (7), 108 (15), 97 (72), 92 (35), 80 (10), 65 (5.5) Anal. For $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$ Calcd. C, 62.06; H, 5.21; N, 12.06%. Found: C, 62.04; H, 5.2; N, 12.0%.

2-[7-Bromo-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4g). 4.868 g (79%) mp 262–266°C, IR (ν_{max}): 2990 cm^{-1} (–OH), 1750 cm^{-1} (–CO), 1670 cm^{-1} (–CO), 1644 cm^{-1} (–CN), 1271, 983, 710 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.5 (t, 2H, $J=2$ Hz, 1H, CH), 5.0 (d, $J=2$ Hz, 2H, CH_2), 7.9 (m, 1H, CH), 6.8 (d, $J=5$ Hz, 1H, CH) ^{13}C NMR (125 MHz, D_2O) 176, 160, 165 (2C), 72, 135, 105, 115, 123 (2C), 146. GCMS (IE, m/z): 281 (81), 283 (82), 220 (1.2), 201 (2), 185 (4), 156 (6), 146 (1.2), 125 (1.2), 120 (100), 108 (16), 97 (39), 92 (58), 78 (8) Anal. For $\text{C}_{10}\text{H}_7\text{BrN}_2\text{O}_3$ Calcd. C, 42.43; H, 2.49; Br, 28.23; N, 9.90%. Found: C, 42.41; H, 2.48; Br, 28.2; N, 9.8%.

2-[7-Bromo-9-methyl-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4h). 4.8 g (76%) mp 265–267°C, IR (ν_{max}): 3010 cm^{-1} (–OH), 1748 cm^{-1} (–CO), 1668 cm^{-1} (–CO), 1644 cm^{-1} (–CN), 1271, 983, 690 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.4 (t, 2H, $J=7.5$ Hz, 1H, CH), 5.0 (d, $J=2$ Hz, 2H, CH_2), 7.82 (s, 1H, CH), 7.80 (s, 1H, CH), 2.1 (s, 3H, CH_3) ^{13}C NMR (125 MHz, D_2O) 176, 162, 166, 122, 72, 132, 105, 124, 145, 15, 152. GCMS (IE, m/z): 295 (74), 297 (77), 305 (33), 295 (17), 278 (8), 120 (100) Anal. For $\text{C}_{11}\text{H}_9\text{BrN}_2\text{O}_3$ Calcd. C, 44.47; H, 3.05; Br, 26.89; N, 9.43%. Found: C, 44.45; H, 2.9; Br, 26.7; N, 9.3%.

2-[7-Bromo-8-methyl-2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene]acetic acid (4i). 4.7 g (70%) mp 270–271°C, IR (ν_{max}): 3012 cm^{-1} (–OH), 1750 cm^{-1} (–CO), 1667 cm^{-1} (–CO), 1645 cm^{-1} (–CN), 1272, 981, 694 cm^{-1} . ^1H NMR (500 MHz, D_2O) 6.4 (s, 2H, $J=2$ Hz, 1H, CH), 5.0 (d, $J=2$ Hz, 2H, CH_2), 7.9 (s, 1H, CH), 6.8 (s, 1H, CH), 2.3 (s, 3H, CH_3) ^{13}C NMR (125 MHz, D_2O) 176, 162, 166, 122, 72, 135, 109, 22, 113, 157. GCMS (IE, m/z): 296, 295 (74), 297 (77), 305 (33), 295 (17), 278 (8), 120 (100) Anal. For $\text{C}_{11}\text{H}_9\text{BrN}_2\text{O}_3$ Calcd. C, 44.47; H, 3.05; Br, 26.89; N, 9.43%. Found: C, 44.5; H, 2.9; Br, 26.8; N, 9.4%.

General procedure 5. A mixture of 2-oxo-2H-pyrido[1,2-a]pyrimidin-3(4H)-ylidene acetic acid and polyphosphoric acid was refluxed in a steam bath for 2–3 h under exclusion of moisture. Thereafter, the reaction mixture was cooled and poured into crushed ice and was neutralized with strong ammonia solution. A white precipitate settled down that was filtered and washed with ice-cold water. The crude product thus obtained was dried and crystallized with pet ether to yield pure white needles.

Pyrido[1,2-a][1,3]diazepin-2(5H)-one 5a. 1.1 g (53%) mp 136°C, IR (ν_{max}): 1668 cm^{-1} (–CO), 1644 cm^{-1} (–CN), 1110 cm^{-1} . ^1H NMR (500 MHz, D_2O) 7.2 (dd, 1H, $J=2$ Hz, 1H, CH), 6.2 (dt, $J=6$ Hz, 1H, CH), 4.6 (t, $J=2$ Hz, 2H, CH_2), 7.7 (dd, $J=7$ Hz, 1H, CH), 6.9 (m, 1H, CH), 8.4 (dd, $J=8$ Hz, 1H, CH) ^{13}C NMR (125 MHz, CDCl_3) 52, 113, 119, 128, 137, 144, 147, 151, 170. GCMS (IE, m/z): 160 (30), 133 (4), 131 (45), 119 (10), 106 (2), 104 (100), 80 (1), 78 (90), 68 (10), 66 (10), 53 (28) Anal. For $\text{C}_9\text{H}_8\text{N}_2\text{O}$ Calcd. C, 67.49; H, 5.03; N, 17.49%. Found: C, 67.50; H, 4.82; N, 17.0%.

6-Methyl-pyrido[1,2-a][1,3]diazepin-2(5H)-one 5b. 1 g (45%) mp 136°C, IR (ν_{max}): 1664 cm^{-1} (–CO), 1638 cm^{-1} (–CN), 1112 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) 7.2 (dt, 1H, $J=6$ Hz, 1H, CH), 6.3 (dt, $J=6$ Hz, 1H, CH), 4.7 (t, $J=2$ Hz, 2H, CH_2), 7.6 (t, $J=8$ Hz, 1H, CH); 8.24 (d, $J=8.4$ Hz, 1H, CH), 2.5 (s, 3H) ^{13}C NMR (125 MHz, CDCl_3) 19, 73, 111, 112, 123.6, 145, 156.5, 148, 162, 166, 175.4. GCMS (IE, m/z): 175 (11), 174 (68), 146 (22), 145 (100), 93 (70), 66 (21), 65 (46), 64 (10), 52 (12) Anal. For $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ Calcd. C, 68.95; H, 5.79; N, 16.08%. Found: C, 68.50; H, 5.6; N, 16.0%.

7-Methyl-pyrido[1,2-a][1,3]diazepin-2(5H)-one 5c. 1 g (45%) mp 137°C IR (ν_{max}): 1670 cm^{-1} (–CO), 1640 cm^{-1} (–CN), 1007 cm^{-1} . ^1H NMR (500 MHz, D_2O) 7.2 (dd, 1H, $J=2.5$ Hz, 1H, CH), 6.3 (dt, $J=6$ Hz, 1H, CH), 4.7 (t, $J=2$ Hz, 2H, CH_2), 7.5 (dd, $J=8.5$ Hz, 1H, CH), 8.1 (d, $J=2$ Hz, 1H, CH), 8.4 (d, $J=8.5$ Hz, 1H, CH), 2.4 (s, 3H) ^{13}C NMR (125 MHz, CDCl_3) 17.7, 52.3, 112.8, 128.5, 128.7, 138.6, 143.8, 147.4, 149.45, 170.27. GCMS (IE, m/z): GCMS (IE, m/z): 175 (11), 174 (68), 146 (22), 145 (100); 93 (70), 66 (21), 65 (46), 64 (10), 52 (12). For $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ Calcd. C, 68.95; H, 5.79; N, 16.08%. Found: C, 68.55; H, 5.6; N, 16.0%.

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