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Electro-organic Reactions. Part 49. The Synthesis and Stereoselective Electrochemical Hydroxylation of 2,3-Dihydro-4*H*-furo[2,3-*d*]pyrido[1,2-*a*]pyrimidin-4-ones

James H. P. Utley,* Mikhail Elinson, Mustafa Güllü, Ralf Ludwig and Majid Motevalli

Department of Chemistry, Queen Mary and Westfield College (University of London), Mile End Road, London E1 4NS, UK

Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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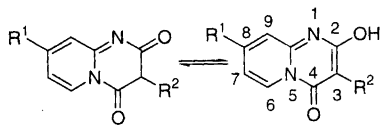
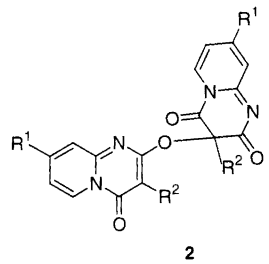
Attempted electrochemical (anodic) hydroxylation of pyridopyrimidine derivatives in the pyridine ring, using trifluoroacetate as nucleophile, fails because enol forms predominate which undergo anodic C–O coupling. Substitution, aimed at precluding enolisation, led to an alternative tautomerisation to 8-methyl-3-alkylmethylene-4*H*-pyrido[1,2-*a*]pyrimidine-2,4-diones which in acidic solution are converted into the title compounds. The 8-methyl-2,3-dihydro-4*H*-furo[2,3-*d*]pyrido[1,2-a]pyrimidine-4-ones are novel and have been fully characterised by spectroscopy and X-ray crystallography. They are electroactive and are oxidised anodically in trifluoroacetic acid–dichloromethane–triethylammonium trifluoroacetate solutions to give the corresponding 3-hydroxy derivatives in good yield. Several examples of this allylic substitution reaction are presented; for cases disubstituted at the 2-position (R^1,R^2) diastereoselective hydroxylation with d.e. ca. 50% (3:1) is observed in which preferential nucleophilic attack on the stabilised intermediate allylic cation occurs at the least hindered face. The stereochemistry of the 3-hydroxy derivatives was assigned by NOE experiments.

Anodic oxidation[1] of pyridopyrimidines **1**, in CF_3CO_2H–CH_2Cl_2–$Et_3NHO_2CCF_3$ (TFA–CH_2Cl_2–$Et_3NH^+TFA^-$), gives not the expected ring-substituted product but high yields of the 1 F oxidation products **4**. These arose from C–O coupling of the radicals **5** generated by anodic oxidation and deprotonation of the corresponding enols with subsequent C–O coupling to **2** which hydrolyses to **3** with consequent decarboxylation. Work-up with methanol gave[1] the methyl ester of **3**. Thus **1b** is an effective representation for our purposes of the pyridopyrimidine structures.

Appropriate substitution (e.g. dialkylation at C-3) should prevent enolisation and, arguably, force anodic substitution into the pyridine ring. In the event it did not prove possible to prepare pyridopyrimidines with such substitution. However, a new series of heterocycles has been discovered and characterised (the 2,3-dihydro-4*H*-furo[2,3-*d*]pyrido[1,2-*a*]pyrimidin-4-ones **6**), which have interesting electrochemical reactivity. In particular they allow a detailed examination of anodic hydroxylation at the allylic position (C-4) and this is shown to be stereoselective in an understandable way. For convenience the parent ring structure for **6**, with numbering, is included in the formulae.



1a **1b**



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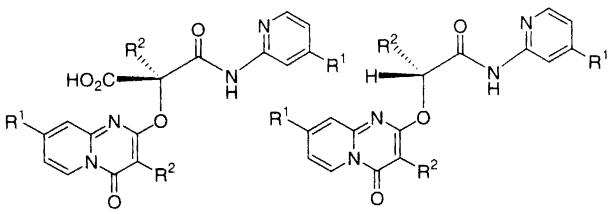
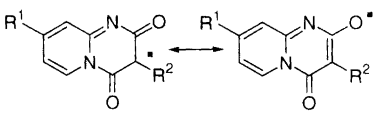
* To whom correspondence should be addressed.



3 4

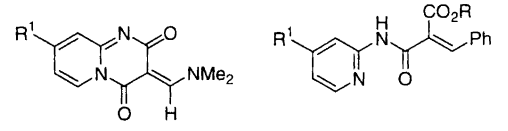


5

6

(**6**, parent ring system, 4*H*-furo[2,3-*d*]pyrido[1,2-*a*]pyrimidine)

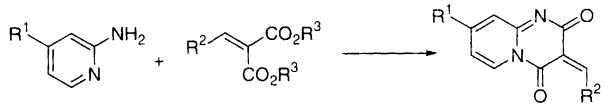
7 8



9 (**11**, R = 2,4,6-trichlorophenyl)

Results and discussion

*Attempted synthesis. 3-Arylmethylene-4*H*-pyrido[1,2-a]pyrimidine-2,4-diones* **7**. Chichibabin[2] reported that dialkyl diethylmalonates failed to condense with 2-aminopyridine to give the expected dicarbonyl derivatives **8**. However, there is a report[3] of successful reaction between 2*H*-pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-dione and $HCONMe_2$–$POCl_3$ to give compounds of structures **9**. Such a system would fulfil our requirement that enolisation is precluded and the syntheses of compounds **7** were attempted by condensation between esters of arylmethylenemalonic acid and 2-aminopyridines (Scheme 1). The methylenemalonates **10** were easily prepared (Scheme 1) by Knoevenagel condensation between dialkylmalonates and aryl aldehydes (see the Experimental section); the bis(2,4,6-trichlorophenyl) esters were made by first hydrolysing the corresponding diethyl malonate and re-esterifying with 2,4,6-trichlorophenol. The trichlorophenyl esters have been shown[1] to be much more reactive in the condensations with 2-aminopyridines.



(**10**, R^1 = H, alkyl, R^2 = alkyl, aryl; R^3 = ethyl, 2,4,6-trichlorophenyl) **7**

Scheme 1. Attempted preparation of 3-arylmethylene-4*H*-pyrido[1,2-*a*]pyrimidine-2,4-diones **7**.

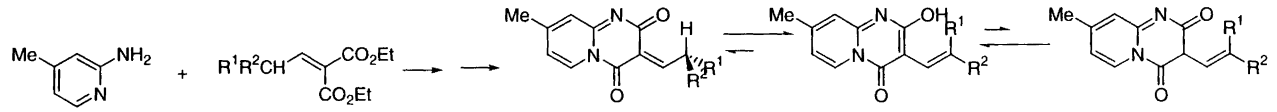
The condensation between 4-methyl-2-aminopyridine and bis-(2,4,6-trichlorophenyl) benzylidenemalonate (**10**, R^2 = Ph, R^3 = 2,4,6-trichlorophenyl) was attempted using the optimum conditions already established,[1] i.e. with triethylamine as a catalyst. Condensation was incomplete, giving only the monoamide **11**. More vigorous attempts included the heating together, without solvent, of 2-aminopyridine and diethyl benzylidenemalonate at 190 °C; only an intractable yellow solid was obtained which was not found to be soluble in any of a range of common solvents. Similar products were obtained from condensations using as starting materials alkyl-substituted 2-aminopyridines and arylidenemalonates containing alkyl substituents on the aryl ring; these might have been expected to yield more soluble products.

*8-Methyl-3-alkylmethylene-4*H*-pyrido[1,2-a]pyrimidine-2,4-diones* **13**. In contrast with the above, the use of diethyl alkylmethylenemalonates **12** as starting materials gave compounds **13** in moderate to high yields. These are not the expected derivatives, **7**, but the products of a rearrangement involving movement of the exocyclic double bond. These results are summarised in Table 1 and Scheme 2 together with a rationalisation of the formation of **13** rather than **7**. The characterisation of the products is fully described in the Experimental section.

*2,3-Dihydro-8-methyl-2,2-dialkyl-4*H*-furo[2,3-d]pyrido-[1,2-a]pyrimidin-4-ones* **6**. In acidic solution the cyclisation of compounds **13** to the furan derivatives **6** took place at room temperature in experiments run for 2–15 h (Scheme 3). The products were characterised by the usual spectroscopic methods (Experimental section) with full characterisation of the spirocyclohexyl derivative [**6a**,

Table 1. Preparation of 8-methyl-2-substituted-2,3-dihydro-4*H*-furo[2,3-*d*]pyrido [1,2-*a*]pyrimidin-4-ones **6**

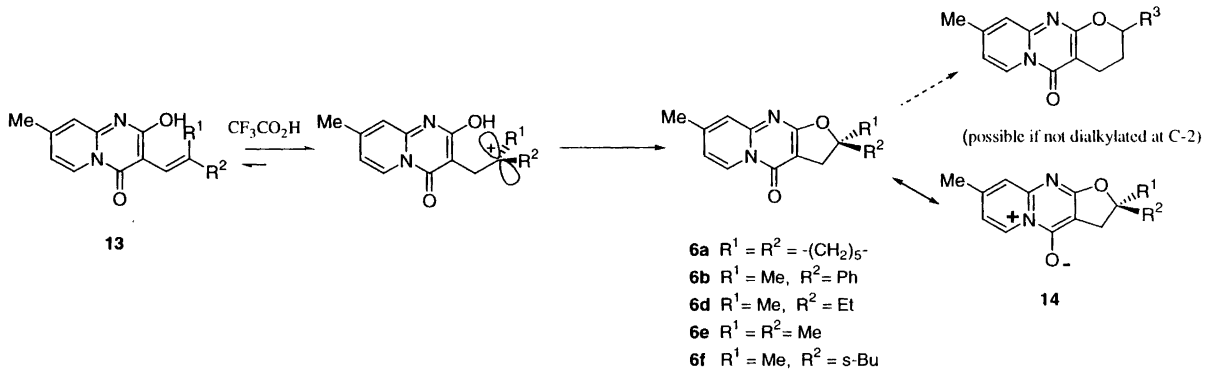
R^1	R^2	Product (% yield)	Product (% yield)
$-(CH_2)_5-$		**13a** (68)	**6a** (99)
Me	Ph	**13b** (65)	**6b** (97)
H	i-Pr	**13c** (42)	—
Me	Et	**13d** (85)	**6d** (91)
Me	Me	**13e** (91)	**6e** (91)
Me	*s*-Bu	**13f** (40)	**6f** (95)



12a $R^1 = R^2 = -(CH_2)_5-$
12b R^1 = Me, R^2 = Ph
12c R^1 = i-Pr, R^2 = H
12d R^1 = Me, R^2 = Et
12e $R^1 = R^2$ = Me
12f R^1 = Me, R^2 = s-Bu (dimethyl ester)

13a $R^1 = R^2 = -(CH_2)_5-$
13b R^1 = Me, R^2 = Ph
13c R^1 = i-Pr, R^2 = H
13d R^1 = Me, R^2 = Et
13e $R^1 = R^2$ = Me
13f R^1 = Me, R^2 = s-Bu

Scheme 2. Preparation of 8-methyl-3-alkylmethylene-4*H*-pyrido[1,2-*a*]pyrimidine-2,4-diones **13**.



13

6a $R^1 = R^2 = -(CH_2)_5-$
6b R^1 = Me, R^2 = Ph
6d R^1 = Me, R^2 = Et
6e $R^1 = R^2$ = Me
6f R^1 = Me, R^2 = s-Bu

(possible if not dialkylated at C-2)

14

Scheme 3. Preparation of 2,3-dihydro-8-methyl-2,2-dialkyl-4*H*-furo[2,3-*d*]pyrido[1,2-*a*]pyrimidin-4-ones **6**.

$R^1 = R^2 = -(CH_2)_5-$] being completed by determination of its structure by X-ray crystallography (see the Experimental section for Fig. 2 and full details, including selected bond lengths and angles).

It appears that dialkylation at C-2 is a prerequisite for efficient cyclisation to the furan derivatives. It may be that cyclisation via a tertiary cation, a consequence of dialkylation at C-2, is greatly favoured. In contrast cyclisation of compound **6c** (R^1 = i-Pr, R^2 = H) would involve a less stable secondary cation. It is also known[4] that furan derivatives with structures similar to **6** can rapidly isomerise under acidic conditions to pyran derivatives; this possibility is included in Scheme 3.

Electrochemical experiments

The formal representation of the structures of the 2,3-dihydro-8-methyl-2,2-dialkyl-4*H*-furo[2,3-*d*]pyrido[1,2-*a*]-pyrimidin-4-ones as **6** still offered hope that the aromaticity of the pyridine ring had been lessened and that structure **14** was not a major contributor. Consequently the electrochemical behaviour of these compounds was explored, initially with a view to anodic hydroxylation of the pyridine ring.

Cyclic voltammetry and controlled potential electrolysis. Examples of compounds of type **6** were found by cyclic voltammetry to be relatively easily oxidised in both TFA–CH_2Cl_2–$Et_3NH^+TFA^-$ and CH_3CO_2H–CH_2Cl_2–$Et_3NH^+CH_3CO_2^-$ and at the modest scan rates used irreversible oxidation was found (Table 2).

The relatively easy oxidation of the enols **13** is as expected by analogy with the electrochemical behaviour of phenols. The practical advantage of the acid–triethylammonium salt electrolyte is that the supporting electrolyte dissociates into its volatile components at relatively low temperatures and is therefore easily removed.[1]

The preparative-scale anodic oxidation of compound **13a** at a platinum anode was problematical; the amount of charge consumed varied from experiment to experiment and the only products isolated (in low yield) were **6a** and **15a**. In the acidic electrolyte the complicating reaction was the relatively rapid cyclisation to **6a**. In contrast, controlled potential electrolysis of examples of compounds **6**, in the trifluoroacetic acid–dichloromethane (1:3) electrolyte at a platinum anode in a divided cell and at the oxidation peak potential, proceeded

Table 2. Cyclic voltammetry:[a] oxidation peak potentials for examples of compounds **13** and **6**

Substrate[b]	R^1	R^2	E_{pa}/V vs. Ag/Ag$^+$
13a	$-(CH_2)_5-$		1.05
6a	$-(CH_2)_5-$		2.0
13e	Me	Me	0.8
6e	Me	Me	2.2

[a] Pt bead, TFA–CH_2Cl_2 (1:3 v/v) $Et_3NH^+TFA^-$ (0.1 M) 0.3 V s^{-1}. [b] See Schemes 2 and 3.

smoothly with the passage of ca. 1.3 F. The product, isolated in 50–60% yield, was the corresponding 2-hydroxy derivative [**13a**, $R^1=R^2=-(CH_2)_5-$]. This reaction turns out to be quite general and the results from related experiments are given in Table 3. The anodic allylic substitution reaction has good literature precedent[5] and the trifluoroacetoxylation variant[6] is valuable because the trifluoroacetate function hydrolyses on work-up.

To find the best reaction conditions a series of electrooxidations of compounds **6b** and **6d** were carried out. These experiments compared constant current and controlled potential electrolysis at varying conversions. In each case TFA–CH_2Cl_2 (1:3) was the solvent with triethylammonium trifluoroacetate (0.1 M) as the supporting electrolyte.

The best results are obtained using a divided cell at constant current with an current density of 4 mA cm^{-2} at a platinum anode. After the consumption of 2.0–2.6 F (see the Experimental section for details) conversion of the starting material into product was over 60% and unreacted starting material was easy to recover by flash chromatography. When the electrolyses were run for longer times only marginally higher yields were obtained together with more side products which were difficult to remove. In one case, the electrolysis of **6d**, the consumption of starting material and the formation of the product **13d** were followed as a function of charge passed. The results of this experiment are shown in Fig. 1.

The oxidation is not completely smooth, otherwise the starting material would be consumed by 2 F (Fig. 1). The departure from ideal behaviour is evidence of competing reactions but the reaction profile confirms that the best yield of product is reached after the passage of about 2 F. As the reaction proceeds the starting material is consumed at less than the theoretical rate so the competing side reactions do not involve consumption of

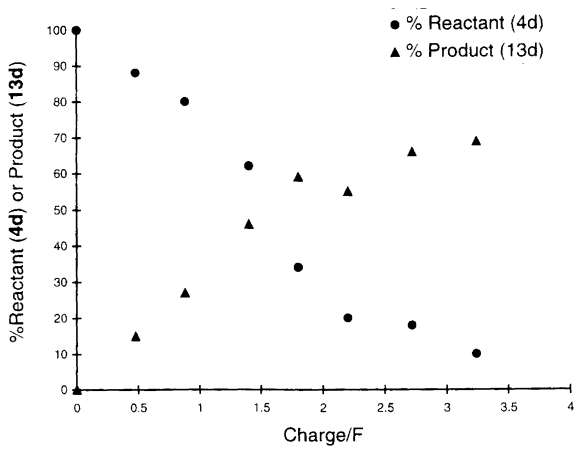


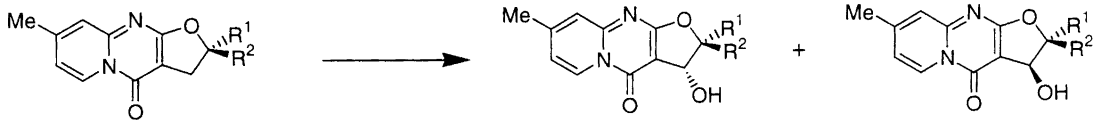
Fig. 1. Anodic hydroxylation of compound **6d**.

starting material. A likely competing reaction is oxidation of the trifluoroacetate anion (a known example of the Kolbe reaction[7]).

The pyridopyrimidine ring system may well be protonated in the acidic electrolyte used but considering that portion of the molecule which is known to be electroactive a plausible reaction path is displayed in Scheme 4. It is likely that the furan ring oxygen is involved in stabilising the allylic cation generated by anodic oxidation. The planarity of such an intermediate causes it to be susceptible to nucleophilic attack at either of two faces. For different substituents R^1 and R^2 there is the possibility of diastereoselective differentiation and this possibility has been explored. The results are included in Table 3 together with reaction conditions and the diastereoisomeric ratios of products as determined by ^1H NMR spectroscopic analysis of crude product mixtures.

Diastereoselective anodic hydroxylation. Although the hydroxylated products **15** are solids it did not prove

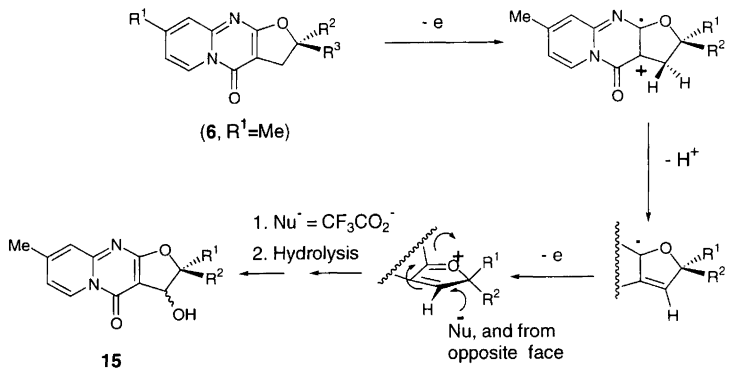
Table 3. Anodic hydroxylation[a] of 2,3-dihydro-8-methyl-2,2-disubstituted-4*H*-furo[2,3-*d*]pyrido[1,2-*a*]pyrimidin-4-ones **6**.



6 (**15** isomer A) (**15**, isomer B)

R^1	R^2	Compound no.	Conversion[b] (%)	Product[c] (% yield)	Isomer ratio (A:B)[d]
$-(CH_2)_5-$		**6a**	98	**15a** (74±4)[e]	—
Me	Ph	**6b**	70	**15b** (67±4)[e]	(3.1±0.1)[e]:1
Me	Et	**6d**	>60	**15d** (76)	(2.0±0.2)[e]:1
Me	Me	**6e**	>60	**15e** (68)	—
Me	*s*-Bu	**6f**	80	**15f** (50)	(3:1)[f]

[a]Divided cell, Pt electrodes, constant current (ca. 4 mA cm^{-2}) passage of 2.0–2.6 F, TFA–CH_2Cl_2 (1:3 v/v)–Et_3N (0.1 M). [b]Overall yield based on starting material consumed. [c]Yield of hydroxylation product allowing for conversion. [d]Assignment of stereochemistry by NOE experiments (see the text). [e]Average of at least two experiments. [f]Because *s*-Bu is a chiral centre the starting material **6f** consists of two diastereoisomers which are seen by ^1H NMR spectroscopy to be in the ratio 1:1. Consequently the electrolysis product (**15f**, R^1=Me, R^2=*s*-Bu) actually consists of four diastereoisomers in the ratio 3:3:1:1.



Scheme 4. Rationalisation of stereoselective anodic substitution.

possible to obtain crystals suitable for X-ray crystallographic structural determination. Consequently the assignment of the stereochemistry of the isomers A and B (see Table 3) came from NOE experiments.[8]

Two sets of experiments were crucial to the assignment, the first conducted on a 3:1 mixture of the isomers of 3-hydroxy-2,8-dimethyl-2-phenyl-2,3-dihydro-4*H*-furo[2,3-*d*]pyrido[1,2-*a*]pyrimidin-4-one **15b** and the second on the pure major isomer of 2-ethyl-3-hydroxy-2,8-dimethyl-2,3-dihydro-4*H*-furo[2,3-*d*]pyrido[1,2-*a*]pyrimidin-4-one **15d**. In the first experiment, concentrating on the spectroscopic features of the major isomer, irradiation at the C-3 proton (5.48 ppm) caused an NOE enhancement of 11% for one of the proton signals attributed to the phenyl group. Irradiation of the methyl group signal (1.78 ppm) resulted in a small enhancement (1%) of the C-3 proton. The distance between the C-3 proton and one of the *ortho*-protons of the phenyl group is 2.85 Å as given in the minimised energy conformation using a force-field calculation (PC Model, Serena Software). Thus the major isomer is assigned as that with the C-3 proton and the phenyl group on the same side of the ring, i.e. the phenyl group and the hydroxy group are *trans*. Examination of the minor (*cis*) isomer is less conclusive. In this case the calculated separation of the C-3 proton and the closest one of the neighbouring methyl group is only ca. 2.5 Å. But irradiation at the C-3 proton signal (5.55 ppm) did not enhance the signal due to the methyl group (at 1.88 ppm). However the reverse experiment, irradiation at 1.88 ppm, did result in an enhancement of 2.4% in the C-3 proton signal.

The pure major isomer of **15d** was obtained by flash chromatography. Irradiation of the CH_2 signal of the ethyl group (at 1.8 ppm) caused an enhancement of the C-3 proton signal (5.18 ppm) by 9%. Conversely, irradiation at 5.18 ppm produced a 7% enhancement in the ethyl group CH_2 signal and one of 5.4% for the terminal CH_3 group signal at 1 ppm. Force field calculations (PC Model, Serena Software) indicate for this compound a distance of 2.6 Å between the C-3 proton and the CH_2 protons. Thus there is compelling evidence that in each case the major isomer produced is that in which the C-3 hydroxy group has been introduced *trans* to the larger of the groups at C-2. This is entirely consistent with the mechanism set out in Scheme 4, with attack by the trifluoroacetate anion occurring at the least hindered face.

Experimental

Electrochemical experiments. The purification of solvents (for cyclic voltammetric and coulometric experiments), electrolytes, and methods used were as described in earlier papers[9] in the series. Conditions for the experiments are given as footnotes to the tables and a typical anodic hydroxylation experiment is described in detail prior to the description of the products **15**.

Preparative scale electrolyses were run in conventional water-jacketed glass divided cells (anolyte volume ca. 50 cm^3) with magnetic stirring. The divider was of medium porosity sintered glass; the anode was a platinum disc (area *ca.* 6.25 cm^2) and the secondary electrode was a carbon rod.

Instrumentation. The following instruments were used: ^1H NMR (Bruker WP80 or AM250); FTIR (Perkin Elmer 1600); mass spectrometry (Kratos MS50RF/Kratos DS90 data system). The X-ray crystallographic data were collected using an Enraf–Nonius CAD 4-circle diffractometer. Cyclic voltammetry was conducted using a QMW-constructed combined waveform generator/potentiostat and controlled potential and controlled current experiments used a Hi-Tec Model DT2101 potentiostat/galvanostat.

Starting materials and products. Syntheses of the alkylmethylenemalonates and arylmethylene malonates **12**. Acetic acid (5 mmol, 0.25 g) and piperidine (15 mmol, 1.28 g) were reacted in a flask fitted with a Dean–Stark trap and a reflux condenser to form piperidinium acetate. Diethyl malonate (100 mmol, 16 g), aldehyde (100 mmol) and dry benzene or xylene were added and the mixture refluxed until no more water was collected. After the mixture had been cooled, the solution was washed (H_2O, 2×40 cm^3), 1 M hydrochloric acid (2×40 cm^3), saturated sodium bicarbonate (2×40 cm^3)

and water ($2 \times 40\ cm^3$). The organic layer was dried ($MgSO_4$) and the solvent removed. Products were generally purified by vacuum distillation.

Diethyl cyclohexylmethylenemalonate **12a**. (Yield, 81%) b.p. 120–125 °C/0.6 mmHg. IR: ν_{max}(liq.)/cm^{-1} 2967, 2844, 1740–1705 (C=O), 1644, 1376. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.1–1.48 (10 H, m, $3 \times CH_2$ and $2 \times CH_3$), 1.52–1.92 (4 H, m, $2 \times CH_2$), 2.08–2.65 (1 H, m, CH), 4.10–4.48 (4 H, m, $2 \times CH_2$), 6.80 (1 H, d, *J* 10, –CH=). MS: *m/z* 254.152 (M^+, 4.9%, $C_{14}H_{22}O_4$ requires 254.152), 208.1 (15), 162 (100).

Diethyl 2-phenylpropylidenemalonate **12b**. (Yield, 55%) b.p. 139–143 °C/0.9 mmHg. IR: ν_{max} (liq.)/cm^{-1} 3029, 2980, 2937, 1725, 1647, 1493, 1451, 1370, 1242. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.18–1.50 (9 H, m, $3 \times CH_3$), 3.75–4.02 (1 H, m, CH), 4.10–4.48 (4 H, m, $2 \times CH_2$), 6.98 (1 H, d, *J* 10, –CH=), 7.29 (5 H, s, Ph). ^{13}C NMR: (250 MHz, $CDCl_3$): δ 14.1, 14.2, 20.3, 39.6, 61.4, 127.0, 127.2, 128.8, 142.6, 151.8, 164.1, 165.5.

Diethyl 3-methylbutylidenemalonate **12c**. (Yield, 82%) b.p. 94–96 °C /1.1 mmHg. IR: ν_{max} (liq.)/cm^{-1} 2961, 2873, 1732 (C=O), 1647, 1466, 1375, 1257, 1214. ^{1}H NMR (80 MHz, $CDCl_3$): δ 0.93 (6 H, d, *J* 7, $2 \times CH_3$), 1.18–1.43 (6 H, m, $2 \times CH_3$), 1.55–2.05 (1 H, m, CH), 2.09–2.28 (2 H, m, CH_2), 4.07–4.43 (4 H, m, $2 \times CH_2$), 7.00 (1 H, t, *J* 10, –CH=).

Diethyl 2-methylbutylidenemalonate **12d**. (Yield, 90%) b.p. 94–96 °C/1.7 mmHg. IR: ν_{max} (liq.)/cm^{-1} 2966, 1728 (C=O), 1646, 1243, 1214, 1058. ^{1}H NMR (80 MHz, $CDCl_3$): δ 0.86 (3 H, t, *J* 7,CH_3), 1.05 (3 H, d, *J* 7, CH_3), 1.20–1.71 (6 H, m, $2 \times CH_3$), 2.18–2.65 (1 H, m, CH), 4.09–4.42 (4 H, m, $2 \times CH_2$), 6.74 (1 H, d, *J* 10, CH=)

Diethyl 2-methylpropylidenemalonate **12e**. (Yield, 87%) b.p. 79–81 °C/0.7 mmHg. IR: ν_{max} (liq.)/cm^{-1} 2969, 2938, 1728 (C=O), 1646, 1468, 1374, 1248, 1218. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.10 (6 H, d, *J* 7, $2 \times CH_3$), 1.25 (3 H, t, *J* 7,CH_3), 1.29 (3 H, d, *J* 7, CH_3), 2.48–2.95 (1 H, m, CH), 4.11–4.52 (4 H, m, $2 \times CH_2$), 6.79 (1 H, d, *J* 10, CH=). MS: *m/z* 214.120 (M^+, 2.5%, $C_{11}H_{28}O_4$ requires 214.120), 169 (25), 123 (31), 122 (100).

Dimethyl 2,3-dimethylpentylidinemalonate **12f**. (Yield, 70%) b.p. 142–144 °C /14 mmHg. IR: ν_{max} (liq.)/cm^{-1} 2961, 2878, 1730 (C=O), 1645, 1436, 1368, 1244, 1219. ^{1}H NMR (80 MHz, $CDCl_3$): δ 0.8–1.0 (3 H, t, CH_3), 0.9–1.0 (6 H, 2 d, *2* x CH_3), 1.0–1.5 (3 H, m, CH_2 and CH), 2.2–2.5 (1 H, m, CH), 3.70 and 3.75 (6 H, $2 \times$ s, $2\ CH_3O$), 6.9 (1 H, d, *J* 11, CH=). MS: *m/z* 228.1 (M^+, 0.5%), 197.1 (9.2), 164.1 (79), 140 (73), 108 (100).

Condensation of the methylenemalonates with 2-amino-4-methylpyridine. The substituted diethyl malonate **12** (10 mmol) and 2-amino-4-methylpyridine (1.3 g, 12 mmol) were dissolved in ethanol (5 cm^3) and heated at 175 °C until the distillation of ethanol from the mixture was complete (ca. 1.5–2.5 h). After cooling, the residue was mixed with cold ethanol, filtered and the solid product washed with ethanol and dried under vacuum.

3-Cyclohexylidenemethyl-2-hydroxy-8-methyl-4H-pyrido-[1,2a]pyrimidin-4-one **13a**. (Yield, 68%), m.p. 294 296 °C. IR: ν_{max} (KBr)/cm^{-1} 3100, 2920, 2840, 2800–2300br, 1685, 1640, 1600, 1572, 1507. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.65 (6 H, br, $3 \times CH_2$), 2.00–2.52 (4 H, br, $2 \times CH_2$), 2.55 (3 H, s, CH_3), 5.97 (1 H, s, CH=), 7.06 (1 H, d, *J* 8, 7-H), 7.42 (1 H, br s, 9-H), 9.06 (1 H, d, *J* 8, 6-H). MS: *m/z* 270.137 (M^+, 43.6%, $C_{16}H_{18}N_2O_2$ requires 270.137), 189 (100), 135 (41), 92 (35). Found: C, 70.92, H, 6.57, N, 10.34, $C_{16}H_{18}N_2O_2$ requires C, 71.10, H, 6.66, N, 10.37%.

2-Hydroxy-8-methyl-3-(2-phenylprop-1-enyl)-4H-pyrido-[1,2-a]pyrimidin-4-one **13b**. (Yield, 65%), m.p. 270–272 °C). IR: ν_{max}/cm^{-1} 2800–2300br (enolic OH), 1685 (C=O, amide), 1650 (C=O, amide), 1608, 1580, 1514, 1475, 1445, 1329, 1371. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.15 (3 H, s, CH_3), 2.50 (3 H, s, CH_3), 6.68 (1 H, s, CH=), 7.06 (1 H, d, *J* 8, 7-H), 7.25–7.72 (6 H, m, 9-H and Ph), 9.10 (1 H, d, *J* 8, 6-H). MS: *m/z* 292.1 (M^+, 100%), 189 (49), 135 (76), 108 (32).

2-Hydroxy-8-methyl-3-(3-methyl but-1-enyl)-4H-pyrido-[1,2-a]pyrimidin-4-one **13c**. (Yield, 42%), m.p. 254–258 °C. IR: ν_{max}/cm^{-1} 3070–2350, 1665, 1598, 1494, 1389. ^{1}H NMR 1.13 (6 H, d, *J* 7, $2 \times CH_3$), 2.49–2.62 (1 H, m, CH), 2.56 (3 H, s, CH_3), 6.70 (1 H, dd, *J* 1 and 16, CH=), 6.99 (1 H, dd, *J* 7 and 16, CH=), 7.06 (1 H, dd, *J* 1 and 8, 7-H), 7.36 (1 H, br s, 9-H), 9.06 (1 H, d, *J* 8, 6-H).

2-Hydroxy-8-methyl-3-(2-methylbut-1-enyl)-4H-pyrido-[1,2-a]pyrimidin-4-one **13d**. (Mixture of *cis* and *trans* compound **13d**) (Yield, 85%), m.p. 259–262 °C). IR: ν_{max}/cm^{-1} 2966, 2840, 2890–2300br, 1672, 1655, 1625, 1584. ^{1}H NMR (250 MHz, $CDCl_3$): δ (1.04 (0.75 H, t, *J* 7, CH_3), 1.13 (2.25 H, t, *J* 7, CH_3), 1.67 (2.25 H, d, *J* 1, CH_3), 1.90 (0.75 H, d, *J* 1, CH_3), 2.08 (0.5 H, q, *J* 7, CH_2), 2.24 (2.5 H, q, *J* 7, CH_2), 2.48 (3 H, s, CH_3), 5.91 (0.25 H, br s, CH=), 5.98 (0.75 H, br s, CH=), 6.95–7.03 (1 H, m, 7-H), 7.35 (1 H, br s, 9-H), 8.98 (1 H, d, *J* 8, 6-H)

2-Hydroxy-8-methyl-3-(2-methylprop-1-enyl)-4H-pyrido-[1,2-a]pyrimidin-4-one **13e**. (Yield, 91%), m.p. 280–285 °C. IR: ν_{max}/cm^{-1} 3045–2100, 1686, 1614, 1579, 1513, 1476, 1367. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.73 (3 H, d, *J* 1, CH_3), 2.00 (3 H, d, *J* 1, CH_3), 2.55 (3 H, s, CH_3), 6.02 (1 H, br s, CH=), 7.06 (1 H, d, *J* 8, 7-H), 7.41 (1 H, br s, 9-H), 9.10 (1 H, d, *J* 8, 6-H). MS: *m/z* 230.106 (M^+, 100%, $C_{13}H_{14}N_2O_2$ requires 230.106), 215

(41), 189 (16), 135 (90), 108 (30). Found: C, 67.80, H, 5.98, N, 12.18, $C_{13}H_{14}N_2O_2$ requires C, 67.82, H, 6.08, N, 12.18%.

2-Hydroxy-8-methyl-3-(2,3-dimethylpent-1-enyl)-4H-pyrido[1,2-a]pyrimidin-4-one **13f**. (Yield, 40%), m.p. 263–265 °C. IR: ν_{max}/cm^{-1} 2960, 2925, 2800–2300br (enolic OH), 1688 (C=O, amide), 1651 (C=O, amide) 1612, 1578, 1511, 1476, 1407, 1368, 1267. ^1H NMR (80 MHz, $CDCl_3$): δ 1.0 (3 H, t, *J* 7, CH_3), 1.2 (3 H, d, *J* 7, CH_3), 1.3–1.6 (2 H, m, CH_2), 1.8 (3 H, s, CH_3), 2.2–2.7 (1 H, m, CH), 2.6 (3 H, s, 8-CH_3), 6.0 (1 H, s, CH=), 7.0 (1 H, d, *J* 8, 7-H), 7.4 (1 H, s, 9-H), 9.1 (1 H, d, *J* 8, 6-H). MS: *m/z* 272.2 (M^+, 17%), 243.1 (32), 189 (100), 135 (55), 109 (42), 108 (42), 92 (45). Found C 70.54, H 7.18, N 10.52, $C_{16}H_{20}N_2O_2$ requires C 70.56, H 7.40, N 10.27.

Cyclisation of the 3-(2,2-dialkylethenyl)-2-hydroxy-8-methyl-4H-pyrido[1,2-a]pyrimidin-4-ones **13** *in the presence of trifluoroacetic acid.* A solution of compounds **13** (1 g) in trifluoroacetic acid–dichloromethane 1:1 mixture (10 cm^3) was stirred at room temperature for 2–24 h. The solution was concentrated under reduced pressure to an oily residue, which was treated with 50 cm^3 of ice–water mixture and neutralised with saturated sodium carbonate to pH 7–8. The precipitated organic products **6** were extracted into dichloromethane, washed (H_2O), and dried ($MgSO_4$). Products were purified by flash chromatography using hexane–ethyl acetate (1:20).

8-Methyl-3'H,-4'H-spiro{cyclohexane-1,2'-furo[2,3-d]-pyrido[1,2-a]pyrimidin}-4'-one **6a**. (Yield, 99%), m.p. 157–159 °C. IR: ν_{max}/cm^{-1} (KBr)/cm^{-1} 3062, 2921, 2856, 1707, 1651, 1590, 1511, 1493, 1436, 1337. ^1H NMR (80 MHz, $CDCl_3$): δ 1.31–2.11 (10 H, br, cyclohehane), 2.49 (3 H, s, CH_3), 3.00 (2 H, s, CH_2), 6.94 (1 H, dd, *J* 1 and 8, 7-H), 7.30 (1 H, br s, 9-H), 9.00 (1 H, d, *J* 8, 6-H). ^{13}C NMR: (70 MHz, $CDCl_3$): δ 21.3, 23.0, 25.0, 37.0, 90.0, 92.0, 107.0, 123.0, 127.0, 149.0, 152.0, 156.0, 171.0. MS: *m/z* 270.138 (M^+, 100%, $C_{16}H_{18}N_2O_2$ requires 270.137), 227.1 (8), 189.1 (79), 135.1 (31), 92.1 (33), 65.0 (16).

(±)-2,8-Methyl-2-phenyl-2,3-dihydro-4-H-furo[2,3-d]-pyrido[1,2-a]pyrimidin-4-one **6b**. (Yield, 97%), m.p. 120–122 °C. IR: ν_{max}/cm^{-1} 3058, 2967, 2919, 2859, 1713 (C=O amide), 1650, 1596, 1485, 1385. ^1H NMR (250 MHz, $CDCl_3$): δ 1.88 (3 H, s, CH_3), 2.50 (3 H, s, CH_3), 3.48 (2 H, s, CH_2), 6.95 (1 H, dd, *J* 1 and 8, 7-H), 7.25–7.58 (6 H, m, 9-H and Ph), 8.98 (1 H, d, *J* 8, 6-H). ^{13}C NMR: (62.9MHz, $CDCl_3$): δ 21.4, 30.1, 40.5, 90.2, 91.6, 117.2, 123.6, 124.4, 127.4, 127.5, 128.6, 145.6, 149.4, 152.3, 177.7, 171.0. MS: *m/z*, 292.1 (M^+, 100%), 189.1 (59), 135.1 (33), 108.1 (24), 92.1 (37). Found C, 73.77, H, 5.55, N, 9.49, $C_{18}H_{16}N_2O_2$ requires C, 73.95, H, 5.52, N, 9.58.

(±)-2-Ethyl-2,8-dimethyl-2,3-dihydro-4H-furo[2,3-d]-pyrido[1,2-a]pyrimidin-4-one **6d**. (Yield, 91%), m.p. 144–145 °C. IR: ν_{max}/cm^{-1} 3060, 2971, 2926, 1711, 1653, 1594, 1488. ^1H NMR (250 MHz, $CDCl_3$): δ 1.00 (3 H, t, *J* 7, CH_3), 1.51 (3 H, s, CH_3), 1.84 (2 H, q, *J* 7, CH_2), 2.47 (3 H, s, CH_3), 2.92–3.14 (2 H, m, CH_2), 6.93 (1 H, dd, *J* 1 and 8, 7-H), 7.27 (1 H, br s, 9-H), 8.97 (1 H, d, *J* 8, 6-H). ^{13}C NMR: 8.1, 21.4, 26.3, 34.1, 36.7, 90.6, 92.2, 116.9, 123.4, 127.3, 149.0, 152.3, 171.2. MS: *m/z* 244.121 (M^+, 100%, $C_{14}H_{16}N_2O_2$ requires 244.121), 215 (48), 189 (44), 135 (44), 92 (36). Found C, 68.70, H 6.51, N 11.42, $C_{14}H_{16}N_2O_2$ requires C, 68.83, H 6.60, N 11.47.

2,2,8-Trimethyl-2,3-dihydro-4H-furo[2,3-d]pyrido[1,2-a]-pyrimidin-4-one **6e**. (Yield, 91%), m.p. 135–136 °C. IR: ν_{max}/cm^{-1} 2969, 1717, 1654, 1592, 1498, 1344. ^1H NMR (250 MHz, $CDCl_3$): δ 1.56 (6 H, s, 2 × CH_3), 2.48 (3 H, s, CH_3), 3.06 (2 H, s, CH_2), 6.92 (1 H, dd, *J* 1 and 8, 7-H), 7.29 (1 H, br s, 9-H), 8.97 (1 H, d, *J* 8, 6-H). ^{13}C NMR: 21.4, 28.5, 38.9, 88.0, 92.1, 117.0, 123.4, 127.3, 149.0, 152.3, 155.9, 171.0. Found C, 67.92, H, 6.16, N, 12.04, $C_{13}H_{14}N_2O_2$ requires C, 67.82, H, 6.08, N, 12.18.

(±)-2,8-Dimethyl-2-(1-methylpropyl)-2,3-dihydro-4H-furo[2,3-d]pyrido[1,2-a]pyrimidin-4-one (**6f,** major isomer). (Yield, 95%), m.p. 108–110 °C. IR: ν_{max}/cm^{-1} 2964, 2370, 1711 (C=O amide), 1654, 1592, 1496, 1340. ^1H NMR (250 MHz, $CDCl_3$): δ 0.92–1.04 (6 H, m, 2 × CH_3), 1.43 (3 H, s, 2-CH_3), 1.51–1.84 (3 H, m, CH_2 and CH), 2.48 (3 H, s, 8-CH_3), 2.84–3.18 (2 H, m, CH_2), 6.92 (1 H, dd, *J* 1 and 8, 7-H), 7.30 (1 H, b s, 9-H), 8.97 (1 H, d, *J* 8, 6-H). ^{13}C NMR: 21.2, 23.8, 35.2, 35.5, 44.2, 92.3, 93.7, 117.3, 122.9, 127.1, 149.7, 151.8, 155.7, 170.7. MS: *m/z* 272 (M^+, 52%), 215 (100), 189 (62), 176 (28) 135 (26), 92 (39). Found C, 70.02, H, 7.47, N, 10.15, $C_{16}H_{20}N_2O_2$ requires C, 70.56, H, 7.40, N, 10.27.

X-Ray crystallographic determination of the structure of compound **6a**. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer operating in the ω/2θ scan mode, with graphite-monochromated Mo Kα radiation. The unit-cell parameters were determined by least-squares refinement on positions of 25 automatically centred reflections with $8.1° \leqslant \theta \leqslant 12.2°$. The structure was solved by the direct method using the SHELX-S program package[10] and refined anisotropically (non-H atoms) on F^2 by full-matrix least-squares procedures using the SHELXL-93 package.[11] All hydrogen atoms were calculated geometrically (riding model) using an AFIX command of the SHELX-93 program. There was some difficulty defining the space group ($P2_12_12_1$), since the data are weak. It proved impossible to make a certain assessment, but the present structure (Fig. 2) is the only and unique solution for our data despite having two molecules in the asymmetric unit and a pseudo-relation between the *x* and *z* coordinates.

The key parameters used for this determination are

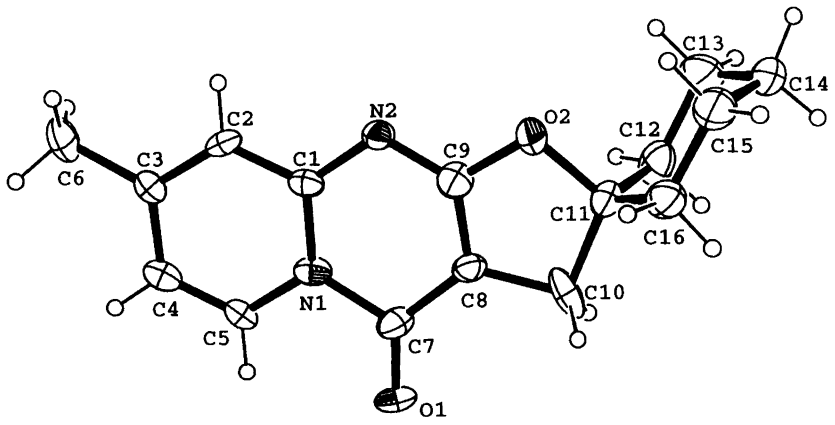


Fig. 2. X-Ray crystallographic structure of compound **6a**.

Table 4. Major experimental parameters for determination of structure **6a**.

Crystal data	Data collection	Refinement
$C_{16}H_{18}N_2O_2$, $M_r = 270.32$	Enraf–Nonius CAD-4 four circle diffractometer	Refinement on F^2
Orthorhombic	$2\theta/\omega$ scan	$R[F > 4\sigma(F)] = 0.0945$
$P2_12_12_1$	$h = -7 \rightarrow 7$	$wR(F^2) = 0.2423$
$a = 7.107(5)$ Å	$k = 0 \rightarrow 14$	$S = 0.1.131$
$b = 12.527(5)$ Å	$l = 0 \rightarrow 32$	2008 reflections
$c = 30.468(11)$ Å	4117 measurements	152 parameters
$V = 2713(2)$ Å^3	2921 independent reflections	H atoms riding with SHELXL93 default geometry
$Z = 8$	424 observed reflections	Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0794P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$
$0.2 \times 0.18 \times 0.16$ mm	$[I > 2\sigma(I)]$	$(\Delta/\sigma)_{max} = -0.267$
Mo Kα radiation	$R_{int} = 0.0806$	$\Delta\rho_{max} = 0.197$ e Å^{-3}
$\lambda = 0.710\,69$ Å	$\theta_{max} = 25.00°$	$\Delta\rho_{min} - 0.302$ e Å^{-3}
Cell parameters from 25 reflections	3 standard reflections	Absolute structure parameter 0.00
$\theta = 8.1$–$12.2°$	Frequency: 60 min	Atomic scattering factors from *International Tables for Crystallography* (1922, Vol. C, Tables 4.26.8 and 6.1.1.4)
$\mu = 0.088$ mm^{-1} $D_x = 1.324$ g cm^{-3}	Intensity variation: none	
D_m not measured		
Colourless, prism		
$T = 290(2)$ K		

displayed in Table 4 and selected bond lengths and angles are given in Table 5.

*Anodic oxidation of 2,3-dihydro-8-methyl-4*H*-furo[2,3-d]pyrido[1,2-a]pyrimidin-4-ones* **6**. For the anolyte freshly distilled triethylamine (0.7 cm^3) was added dropwise to a mixture of trifluoroacetic acid (12 cm^3) and dichloromethane (48 cm^3). The electroactive compounds

Table 5. Selected bond lengths and angles for structure **6a** (NB numbering is for the crystal structure in Fig. 2).

Bond	Length/Å	Bonds	Angle/°
C3–C4	1.399	C5–N1–C1	120.3
C1–C2	1.374	C5–N1–C7	116.1
C1–N1	1.376	C1–N1–C7	123.5
C5–N1	1.346	C9–N2–C1	114.8
C1–N2	1.362	C9–O2–C11	107.8
C7–N1	1.466	N2–C9–C8	128.2
C9–N2	1.315	C9–C8–C7	119.9
C8–C7	1.430	O1–C7–C8	128.7
C8–C9	1.378	O2–C11–C16	107.1
C9–O2	1.343	C7–C8–C10	128.8

(**6**, 1 mmol) were dissolved in the anolyte and electrolysed until between 2 and 2.6 F had been consumed. The anolyte was evaporated to dryness under reduced pressure at room temperature and the residue neutralised with aqueous sodium carbonate solution. The organic materials were extracted into chloroform (5×30 cm^3) and the combined organic layers washed with water (2×30 cm^3) and dried (MgSO4). The solvent was removed and the crude products purified by flash chromatography with hexane–ethyl acetate (1:20). Further details and yields are given in Table 3.

*(±)-3′-Hydroxy-8′-methyl-3′*H*,4′*H*-spiro{cyclohexane-1,2′-furo[2,3-d]pyrido[1,2-a]pyrimidin}-4′-one* **15a**. M.p. 182–185 °C. IR: ν_{max}/cm^{-1} (KBr)/cm^{-1} 3340, 2934, 1694 (C=O amide), 1649, 1590, 1510, 1482, 1455, 1328, 1277. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.28–2.10 (10 H, m, cyclohexane), 2.50 (3 H, s, CH_3), 2.87 (1 H, br s, OH), 5.13 (1 H, s, CH), 6.95 (1 H, dd, *J* 1 and 8, 7-H), 7.28 (1 H, br s, 9-H), 8.96 (1 H, d, *J* 8, 6-H). ^{13}C NMR: 21.5, 22.5, 22.7, 25.2, 29.7, 35.4, 74.2, 92.5, 95.4, 117.2, 123.6, 127.6, 150.3, 153.1, 156.5, 171.2. MS: *m/z* 286.121

(M-1, 2.8%), 239.1 (3), 205.1 (6), 188.1 (67), 135.1 (14), 119 (100), 92.0 (22).

*(±)-3-Hydroxy-2,8-dimethyl-2-phenyl-2,3-dihydro-4*H-*furo[2,3*-d*]pyrido[1,2*-a*]pyrimidin-4-one* **15b**. Mixture of *cis* and *trans* isomers (A and B): m.p. 208–219 °C. IR: ν_{max} (KBr)/cm^{-1} 3371, 3034, 2982, 1702, 1654, 1591, 1490, 1330, 1270. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.78 (0.75 H, s, CH_3), 1.87 (2.25 H, s, CH_3), 2.49 (2.25 H, s, CH_3), 2.49 (0.75 H, s, CH_3), 5.33 (0.25 H, s, CH), 5.47 (0.75 H, s, CH), 6.93–7.04 (1 H, m, 7-H), 7.24–7. 56 (6 H, m, 9-H and Ph), 8.90–9.04 (1 H, m, 6-H).

(±)-trans-*2-Ethyl-3-hydroxy-2,8-dimethyl-2,3-dihydro-4*H-*furo[2,3*-d*]pyrido[1,2*-a*]pyrimidin-4-one* (**15d**, isomer A). M.p. 195–204 °C. IR: ν_{max}/cm^{-1} 3500–3100 (OH), 2974, 2924, 1703, 1652, 1591, 1482. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.00 (3 H, t, *J* 7, CH_3), 1.55 (3 H, s, CH_3), 1.61–1.87 (2 H, m, CH_2), 2.47 (3 H, s, CH_3), 3.28 (1 H, br s, OH), 5.18 (1 H, s, CH), 6.93 (1 H, dd, *J* 1 and 8, 7-H), 7.30 (1 H, br s, 9-H), 8.93 (1 H, d, *J* 8, 6-H). ^{13}C NMR: 7.9, 18.1, 21.5, 29.7, 32.6, 73.8, 94.0, 95.4, 117.2, 123.6, 127.6, 150.3, 153.1, 156.5, 171.3. MS: *m/z* 260.116 (M^+, 38%, $C_{14}H_{16}N_2O_3$ requires 260.116), 188 (100), 160 (56), 113 (53), 92 (58).

*(±)-cis-2-Ethyl-3-hydroxy-2,8-dimethyl-2,3-dihydro-4*H-*furo[2,3*-d*]pyrido[1,2*-a*]pyrimidin-4-one* (**15d**, isomer B). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.14 (3 H, t, *J* 7, CH_3), 1.38 (3 H, s, CH_3), 1.87–2.08 (2 H, m, CH_2), 2.48 (3 H, s, CH_3), 3.12 (1 H, br s, OH), 5.10 (1 H, s, CH), 6.93 (1 H, dd, *J* 1 and 8, 7-H), 7.30 (1 H, br s, 9-H), 8.94 (1 H, d, *J* 8, 6-H).

*(±)-3-Hydroxy-2,2,8-trimethyl-2,3-dihydro-4*H-*furo[2,3*-d*]pyrido[1,2*-a*]pyrimidin-4-one* **15e**. M.p. 199–202 °C. IR: ν_{max}/cm^{-1} 3500–3100 (OH), 2973, 2928, 1702, 1591, 1481, 1329. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.45 (3 H, s, CH_3), 1.60 (3 H, s, CH_3), 2.48 (3 H, s, CH_3), 3.68 (1 H, br s, OH), 5.10 (1 H, s, CH), 6.92 (1 H, dd, *J* 1 and 8, 7-H), 7.29 (1 H, br s, 9-H), 8.90 (1 H, d, *J* 8, 6-H). ^{13}C NMR: 20.8, 21.5, 26.7, 75.0, 91.3, 95.3, 117.2, 123.6, 127.6, 150.3, 153.0, 156.6, 171.1. MS: *m/z* 246.100 (M^+, 69%), 188.1 (100), 159.1 (20), 132.1 (13), 119.1 (8).

*(±)-3-Hydroxy-2,8-dimethyl-2-(1-methylpropyl)-2,3-dihydro-4*H-*furo[2,3*-d*]pyrido[1,2*-a*]pyrimidin-4-one* (**15f**, mixture of isomers). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.89–1.09 (6 H, m, 2 × CH_3), 1.21–1.83 (6 H, m, 2-CH_3, CH and CH_2), 2.48 (3 H, s, CH_3), 3.09–3.21 (1 H, m, OH), 5.05–5.29 (1 H, m, CH), 6.77–6.89 (1 H, m, 7-H), 7.29 (1 H, br s, 9-H), 8.93 (1 H, d, *J* 8, 6-H)

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