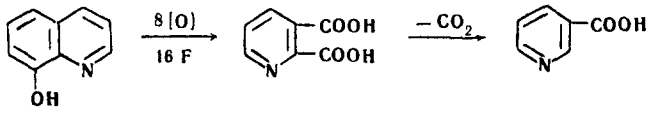
The electrochemical oxidation of quinoline is described in [1–5]; the literature does not contain any information about electrooxidation of 8-hydroxyquinoline. Work on the chemical oxidation of 8-hydroxyquinoline shows that permanganate [6], nitric acid [7–10], or mixed oxygen-ozone oxidation gives quinolinic acid, which is readily decarboxylated to nicotinic acid.

The present communication describes the preparation of nicotinic acid by electrochemical oxidation of 8-hydroxyquinoline:



EXPERIMENTAL

The electrochemical oxidation of 8-hydroxyquinoline was run in a cylindrical electrolyzer with a ceramic diaphragm. The anode was a perforated lead one, previously coated with a layer of lead dioxide by anodic treatment in sulfuric acid. The cathode is also of lead. Working anolyte volume 100 ml, anolyte composition (g/l): 8-hydroxyquinoline 112, sulfuric acid 475; V_2O_5 1; the catholyte was 60% H_2SO_4. Electrolysis conditions: anolyte temperature 75 ± 2°, anode current density 5 amp/dm^2, quantity of electricity passed 125% (theoretical quantity of electricity 16 F per mole of 8-hydroxyquinoline).

After the electrolysis the anolyte was neutralized with 25% NH_4OH, and brought to pH 2. Quinolinic acid was extracted from this solution by n-butanol at 90–95°. When the butanol was distilled off, the quinolinic acid underwent decarboxylation to nicotinic acid, and the latter separated when the remaining small volume of butanol was cooled to 0°. Yield 5.9–6.0 g nicotinic acid, 96–98% pure (60% yield). Recrystallization from water, using decolorizing charcoal, gave nicotinic acid mp 234–236°.

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12 November 1965

All-Union Scientific Research Institute for Chemical Reagents and Very Pure Chemical Substances, Moscow

HYDRAZONES AND HYDRAZIDES OF 4,6-DIMETHYL-5-CARBOXYPYRID-2-ONE AND 4-METHYL-6-CARBOXYMETHYLPYRID-2-ONE

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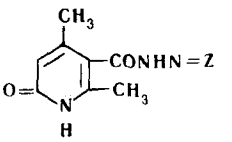
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 168–170, 1967

UDC 547.821.41'823'826.1'556.9

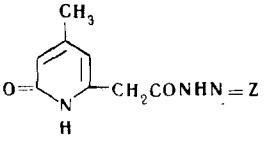
With a view to elucidating antitubercular activity, from the hydrazides of 4, 6-dimethyl-5-carboxypyrid-2-one and 4-methyl-6-carboxymethylpyrid-2-one, are synthesized the hydrazones of acetone, methyl ethyl ketone, acetophenone, benzaldehyde, p-hydroxypropiophenone, p-dimethylaminobenzaldehyde and tetrahydrothiopyr-4-one.

4,6-Dimethyl-5-ethoxycarbonylpyrid-2-one and the isomeric 4-methyl-6-ethoxycarbonylmethylpyrid-2-one, now prepared by us from β-aminocrotonic ester by somewhat modified methods [1, 2], have been used by us to synthesize the corresponding hydrazides (I, II), and a number of hydrazones (III–XI) based on them, with a view to testing their antiturbercular activities.

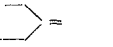


III, IV

III, V	$z=(CH_3)_2C$
IV, VIII	$z=C_6H_5CH$
VI	$z=(CH_3)(C_2H_5)C$
VII	$z=(C_6H_5)(CH_3)C$



V–XI

IX	$z=(p\text{-}HOC_6H_4)(C_2H_5)C$
X	$z=p\text{-}(CH_3)_2NC_6H_4CH$
XI	$z=S$  $=$

EXPERIMENTAL

Hydrazide of 4, 6-dimethyl-5-carboxypyrid-2-one (I). The starting 4, 6-dimethyl-5-ethoxycarbonylpyrid-2-one, mp 136–137°, was pre-

Hydrazones Derived from the Hydrazide of 4-Methyl-6-carboxymethylpyrid-2-one

Compound number	Mp, °C (recrystallization solvent)	Formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
V	229—230 (decomp, MeOH)	$C_{11}H_{15}N_3O_2$	59.53 59.37	6.70 6.83	19.12 19.04	59.71	6.83	18.99	75
VI	171—172 EtOH	$C_{12}H_{17}N_3O_2$	61.12 60.99	7.30 7.34	18.24 18.20	61.25	7.28	17.86	76
VII	206—207 EtOH	$C_{16}H_{17}N_3O_2$	67.69 67.48	5.98 6.09	14.93 15.05	67.82	6.04	14.34	75
VIII	216—217 EtOH	$C_{15}H_{15}N_3O_2$	66.51 66.88	5.76 5.67	15.45 15.48	66.89	5.61	15.61	43
IX	206—207 EtOH	$C_{17}H_{19}N_3O_3$	— —	— —	13.25 13.11	—	—	13.41	44
X	220—221 75% EtOH	$C_{17}H_{20}N_4O_2$	65.29 65.54	6.53 6.53	17.84 17.78	65.36	6.45	17.94	57
XI	229—230 75% EtOH	$C_{13}H_{17}N_3O_2S$**	—	—	15.50 15.39	—	—	15.40	75

*Calculated on the 4-methyl-6-ethoxycarbonylpyrid-2-one.
**Found: S 11.29; 11.18% Calculated for S 11.48%

pared in 42% yield by the method of [1, 2], modified by saturating undistilled aminocrotonic ester in dichloroethane with HCl, then refluxing for 30–40 min. 10.2 g of the resultant ester and 50 ml hydrazine hydrate were refluxed together for 20 hr, the mixture cooled, and 1.5 g (23%) 4, 6-dimethylpyrid-2-one, mp 175–177° filtered off [1]. The filtrate was evaporated, the residue treated with EtOH to give 7.3 g (77%) of sufficiently pure hydrazide, mp 257–258° (ex EtOH). Found: C 52.43, 52.49; H 6.04, 6.02, N 23.48; 23.42%. Calculated for $C_8H_{11}N_3O_2$. C 53.02; H 6.12; N 23.19%.

Isopropylidenehydrazide of 4, 6-dimethyl-5-carboxypyrid-2-one (III). 1.3 g (6 mmole) hydrazide I and 15 ml acetone was boiled for 3 hr, the acetone being gradually distilled off, the acetone removed being made up by dry acetone added from a dropping funnel. Near the end a large part of the acetone was distilled off until crystals of hydrazone appeared. After cooling the precipitate was filtered off, and washed with 3 ml cold MeOH, yield 0.55 g (35%) hydrazone III, mp 288–289° (ex MeOH). Found C 59.71, 59.63; H 6.98, 7.13; N 19.04, 19.12%. Calculated for $C_{11}H_{15}N_3O_2$. C 59.71; H 6.83; N 18.99%.

4, 6-Dimethyl-5-carboxypyr-2-one benzlidenehydrazide (IV). 1.81 g (10 mmole) hydrazide I and 1.06 g (10 mmole) benzaldehyde in 50 ml dry EtOH and 50 ml dichloroethane was boiled, the solvent being distilled off and at the same time a mixture of 150 ml dichloroethane and 50 ml EtOH added. Final distilling off of the solvent gave 1.62 g impure hydrazone, and three recrystallizations of this from MeOH gave 0.35 g (13%) pure compound mp 303° (decomp.). Found: C 67.16, 67.29, H 5.72; 5.69, N 15.67; 15.46%. Calculated for $C_{15}H_{15}N_3O_2$. C 66.89; H 5.61; N 15.61%.

4-Methyl-6-carboxymethylpyrid-2-one (α-methylbenzylidene)-hydrazide (V). The starting 4-methyl-6-ethoxycarbonylmethylpyrid-2-one, mp 166–167°, was prepared in 20% yield as described in [1, 2], but with the modification that distilled crystalline aminocrotonic ester in dichloroethane was saturated with HCl with external water cooling (mixture heated up to about 40°), without further heating of the reaction mixture. 1.95 g ester and 0.7 ml hydrazine hydrate in 25 ml dry EtOH was refluxed for 3 hr, cooled, filtered, to give 1.75 g (97%) hydrazide (mp 189–190°). The latter was converted to hydrazone V by reacting with acetophenone and distilling off of the water, with dichloroethane. Yield 2.4 g (75% on the ester). The table gives information regarding this hydrazone and hydrazones VII–XI prepared similarly. Hydrazones V and VI (see table) were, like hydrazone III, prepared with the modification that the reaction was run in the presence of dry EtOH.

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27 November 1965

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SYNTHESIS OF ESTERS OF N-6-PURINYLAMINO ACIDS

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 170–173, 1967

UDC 547.853+547.89

Reaction of esters of amino acids with 6-chloropurine gives a series of hitherto unknown esters of N-6-purinylamino acids, which are potential kinins. The IR spectra of these compounds are determined to characterize them.

Along with auxins and giberellins, kinins (6-N-substituted aminopurines) are known to participate in regulating exchange of plant substances [1, 2]. Of the kin-