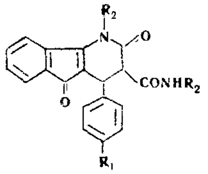

R_1	R_2	Mp, °C (decomp)	Formula	Found, %				Calculated, %				Yield, %
				C	H	N	Cl	C	H	N	Cl	
H	H	258–259	$C_{19}H_{14}N_2O_3$	71.55	4.34	8.80	—	71.68	4.40	8.80	—	91
NO_2	H	254–255	$C_{19}H_{13}N_3O_5$	63.02	3.80	11.71	—	62.81	3.60	11.57	—	85
OCH_3	H	255–257	$C_{20}H_{16}N_2O_4$	69.11	4.79	8.09	—	68.96	4.65	8.04	—	83
Cl	H	233–234	$C_{19}H_{13}N_2O_3Cl$	64.35	3.75	8.10	10.30	64.68	3.71	7.93	10.06	88
H	CH_3	130–132	$C_{21}H_{18}N_2O_3$	73.04	5.30	8.21	—	72.81	5.21	8.09	—	93

Acid hydrolysis of compound II leads to scission of bond 4—4a and formation of β-indandionylhydrocinnamic acid, which has been reported in the literature [7]; this is also formed by acid hydrolysis of III.

EXPERIMENTAL

1-Phenyl-2-carbamido-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-dione (IIa). 5 g I was suspended in 50 ml conc. HCl, and left at room temperature for 24 hr. After some time the mixture turned rose colored. The orange precipitate was separated off, and washed with water, yield 4.3 g. It was recrystallized from EtOH.

Ib–e were synthesized similarly. The table gives the properties of the compounds prepared.

α-(3-Aminoind-2-en-1-one-2-yl)benzylmalonic acid (III). 3 g IIa was dissolved in 50 ml 1 N NaOH, and the mixture heated on a water batch until ammonia evolution ceased. After cooling the solution was acidified, when a red precipitate formed. Yield 2.4 g (70%), mp 173–174° (decomp). In recrystallizing, prolonged boiling has to be avoided, in order to avoid possible changes in the product. Found: C 68.02; H 4.68; N 4.20%. Calculated for $C_{19}H_{15}NO_5$: C 67.75; H 4.45; N 4.15%.

1-Phenyl-1, 2, 3, 4-tetrahydro-4-azafluoren-3, 9-dione (IV). A suspension of 3 g III in 30 ml diethylene glycol was heated at 130–140° until CO_2 evolution was complete, when the reaction products became viscous. The IV formed was separated off, and washed, yield 1.1 g (45%), mp 239–240° (decomp). Found: C 78.35; H 4.64; N 5.07; 5.24%. Calculated for $C_{18}H_{13}NO_2$: C 78.53; H 4.76; N 5.08%.

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CYANOETHYLATION OF TETRAHYDROFURAN

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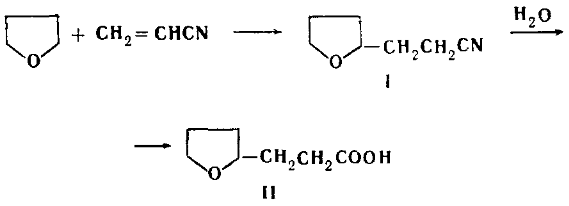
It is shown that it is possible to carry out free radical cyanoethylation of tetrahydrofuran, to give the nitrile of α-tetrahydrofuranpropionic acid in 50–60% yield.

One of us has shown that tetrahydrofuranpropionic acid raises the cotton plant yield if prior to sowing the seeds are wetted with a $5 \cdot 10^{-3}$ to $5 \cdot 10^{-4}$ concentration solution.

The literature [1] describes a 2-stage synthesis of the compound: condensation of furfural with acetic anhydride by the Perkin reaction, followed by reduction of the resultant furylacrylic acid. The method is laborious, and the yield of acid low.

We decided to synthesize the acid by cyanoethylating tetrahydrofuran with acrylonitrile, followed by saponification of the resultant nitrile I. (It is not ruled out that nitrile I, like other nitriles [2] will also be a stimulant of cotton plant growth.) The work was based on previously described reactions of alkylation of tetrahydrofuran and other cyclic ethers of olefins, in the presence of radical catalysts [3, 4], and reactions of addition of unsaturated compounds to compounds with an active hydrogen atom [5–7].



The cyanoethylation of tetrahydrofuran with acrylonitrile was run in sealed glass tubes at 190–210° using tert-butyl peroxide as the catalyst. Cyanoethylation does not take place without a catalyst, neither does it take place at considerably lower temperatures. Despite the large excess of tetrahydrofuran (90:1), polycyanoethyl derivatives, mainly disubstitution ones, were obtained to some extent. It is evident too that the nitrile cut contains various side reaction products as impurities. The yield of crude nitrile is 50–60%. Tetrahydrofuranpropionitrile has not been described in the literature. To obtain information, it was saponified with ethanolic alkali. IR spectra of the resultant, and also of "model" tetrahydrofuranpropionic acid were measured, and found to agree well.

EXPERIMENTAL

Tetrahydrofuranpropionitrile (I). A mixture of 180 ml (2.2 mole) tetrahydrofuran, 1.3 g (0.02 mole) acrylonitrile, and 0.4 g (0.0027 mole) tert-butyl peroxide was heated in sealed tubes at 190–200°, for 2 hr. After distilling off the tetrahydrofuran, the residue was vacuum-fractionated to give 2 g of a 1st cut bp 78–90° (8 mm), and 0.7 g of a 2nd cut bp 95–125° (8 mm). The 1st cut was repeatedly distilled. Bp 92–94° (8 mm); n_D^{20} 1.4468. Found: C 67.10; H 9.20; N 10.85%. Calculated for $C_7H_{11}NO$: C 67.20; H 8.80; N 11.20%. The IR spectrum showed bands at 2260 cm^{-1} (C≡N), 1080 and 1180 cm^{-1} (—C—O—C—).

Tetrahydrofuranpropionic acid (II). 4 g I was refluxed with 2.8 g KOH in 20 ml EtOH for 10 hr. After cooling the products were acidified with dilute HCl, the KCl filtered off, and the EtOH distilled off until the mixture separated into layers. Then the oil was separated off, the water layer thrice extracted with benzene, oil and extracts bulked, dried over anhydrous $MgSO_4$, and distilled. Yield 2 g (45%) tetrahydrofuranpropionic acid, bp 187° (55 mm), n_D^{20} 1.4590 [the literature [1, 8] gives bp 123°–124° (5 mm), n_D^{22} 1.4580], M (Rast) 150.8 (calculated 144).

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