*Syntheses of Kinetin-analogues. II**

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In the previous paper[1] the authors reported the relation between the chemical

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1) F. S. Okumura et al., This Bulletin, **30**, 194 (1957).

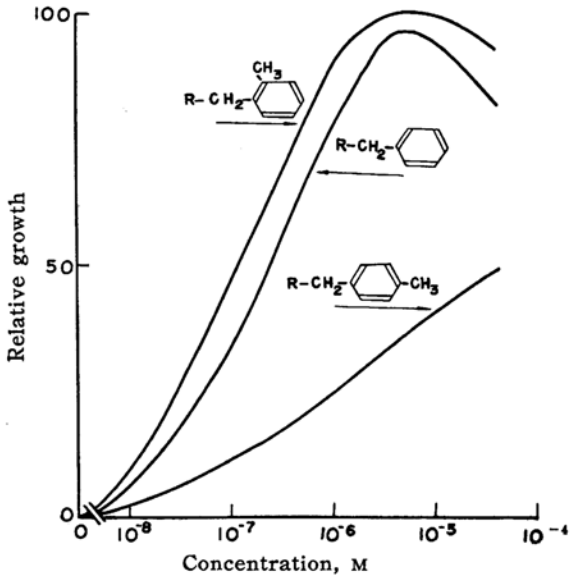

Fig. 1.
R=Aminopurine

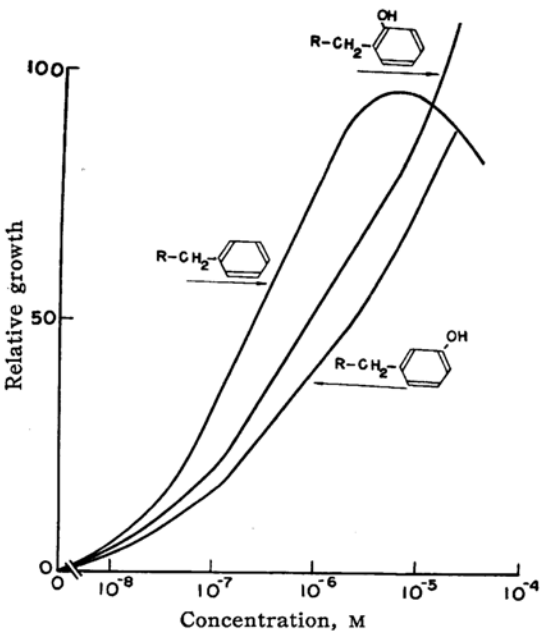

Fig. 2.
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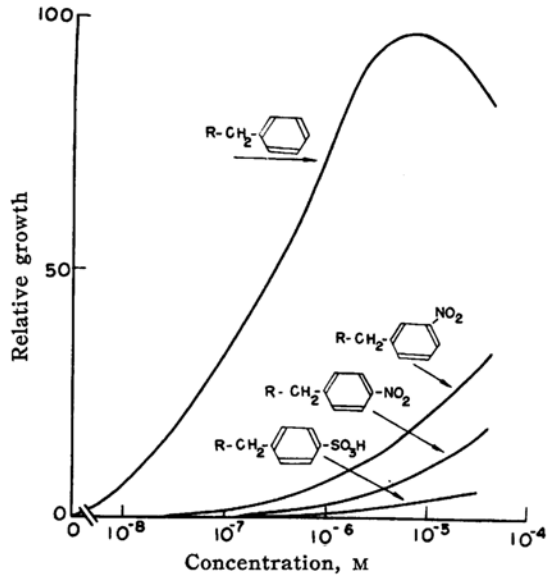

Fig. 3.
R=Aminopurine

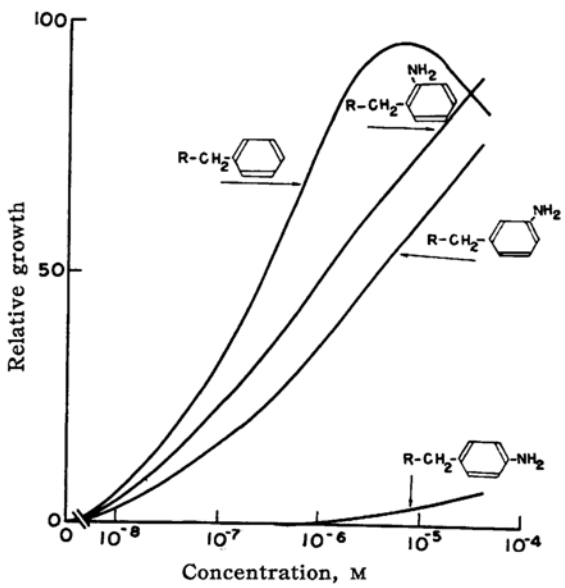

Fig. 4.
R=Aminopurine

structure and the physiological activity of kinetin-analogues by using the leaf test method[2] (*Raphanus sativus L. var. acanthiformis* Makino). It was shown[1] that the kinetin-analogues which have a benzene ring instead of a furan ring have almost the same activity as kinetin on leaf growth.

Seventeen kinetin analogues with various substituents in the benzene ring of 6-(benzylamino)-purine have been synthesized in order to investigate the effect of substituents on leaf growth. Positive and negative substituents, such as methyl, hydroxyl, methoxyl, amino, nitro and sulfonic acid groups were introduced into the ortho, meta or para position of the

2) S. Kuraishi and F. S. Okumura, *Bot. Mag., Tokyo*, **69**, 300 (1956).
3) M. W. Bullock, J. J. Hand and E. L. R. Stockstad, *J. Am. Chem. Soc.*, **78**, 3693 (1956).

TABLE I. SYNTHESES OF SUBSTITUTED 6-(BENZYLAMINO)-PURINES

Substituent	Temp. (°C) and time (hr.) of run		Yield (%)	m.p. (°C)	Analysis N%	
					Found	Calcd.
o-Methyl	130～140[a]	11	67.5	242[b],[e]	29.52	29.27
p-Methyl	130～140[a]	13	65.0	264[c],[e]	29.19	29.27
o-Amino	130～140	5	25.4	279～280[e]	34.81	34.98
m-Amino	120～130	4	49.3	243～244[e]	35.13	34.98
p-Amino	120～130	5	25.2	239～240[e]	35.19	34.98
m-Nitro	130～140	5	34.0	272[e]	31.06	31.15
p-Nitro	90	4	10.3	220～226[d],[e]	29.86	31.15
o-Hydroxy	135	4	23.2	264[h]	29.93	29.04
m-Hydroxy	140～150[a]	18	22.8	284～286[e]	29.20	29.04
m-Methoxy	130～135[a]	13	30.4	248～249[f]	27.46	27.44
o-Chloro	125～130[a]	11	60.8	227～228[e]	27.01	26.97
m-Chloro	130[a]	15	59.0	241～242[e]	26.92	26.97
p-Chloro	120[a]	17	70.5	280～280.5[e]	27.16	26.97
p-Sulfo	160～170	20	12.0	238～242[d],[g]	24.14	22.94

a) in a sealed tube b) 243～244°C[3] c) 263°C[3] d) This compound is still impure.
e) Ethanol f) Methanol g) Water h) Dimethylformamide

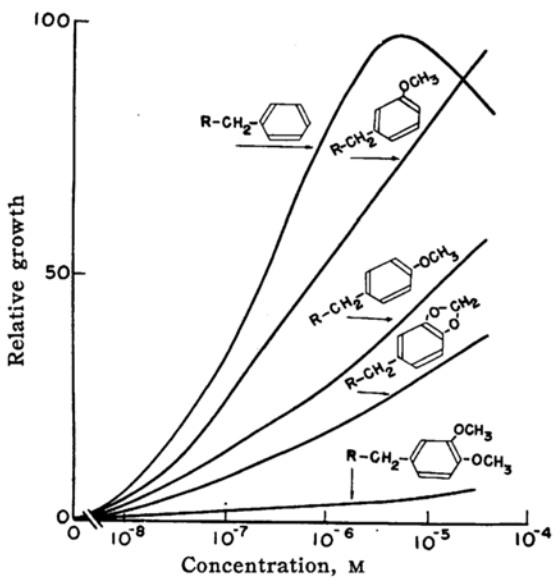

Fig. 5.
R=Aminopurine

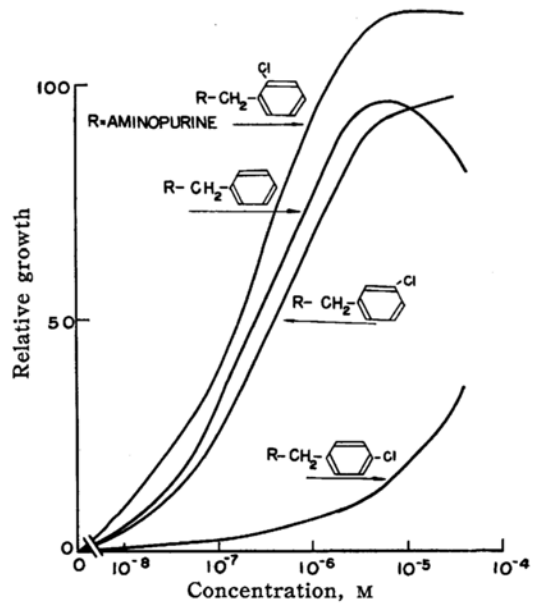

Fig. 6.
R=Aminopurine

benzene ring. In these seventeen analogues, fourteen are new compounds and three have already been reported[1].

The results are shown in Figs. 1, 2, 3, 4, 5 and 6. It is of interest that the ortho substituted isomers are the most active on leaf growth and the activity decreases in the order of the meta and the para isomers. Furthermore, it is noteworthy that the activity of some ortho isomers in higher concentration is stronger than that of 6-(benzylamino)-purine in its optimum concentration, e.g., *o*-methylbenzylaminopurine (Fig. 1), *o*-hydroxybenzylaminopurine (Fig. 2) and *o*-chlorobenzylaminopurine (Fig. 6) and that the kinetin activity is decreased by both meta and para substitution. It is clear from the above facts that the kinetin activity is favored by the ortho-substitution but disfavored by the meta- or para-substitution.

Experimental.—The syntheses of substituted 6-(benzylamino)-purines were achieved by condensing 6-(methylmercapto)purine with various amines. In general, 6-(methylmercapto)-purine was heated with 2 to 3 molecular equivalents of an amine with or without a solvent in a sealed or open tube at the given temperature and for the period given in Table I.

6-(*o*-Chlorobenzylamino)purine.—A mixture of 0.3 g. of 6-(methylmercapto)-purine (3.5 mol.) and 0.87 g. of *o*-chlorobenzylamine (1 mol.) was heated for eleven hours under reflux at 125~130°C. After cooling, the reaction product was precipitated by the addition of acetone, collected, washed with acetone, and then recrystallized from ethanol to give the product, m.p. 227~228°C, in a yield of 60.8%.

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