Tab. II. Verteilung der Radioaktivität nach verschiedener Behandlund der Cicer-Triebe

	Prozent der aufgenommenen Aktivität
Versuch mit Tetrahydroxychalkonglucosid-[β-^{14}C]	
Cicer-Triebe	100
Methanol-Extrakt	67
Rückstand	33
Rückstand nach Extraktion mit Pyridin/Wasser	25
Rückstand nach Hydrolyse im Bombenrohr	18
Versuch mit 7,4'-Dihydroxyflavon-7-glucosid-[2-^{14}C]	
Cicer-Triebe	100
Methanol-Extrakt	40
Rückstand	60
Rückstand nach Hydrolyse im Bombenrohr	24

das Unlösliche aus noch etwas verkrusteter Gerüstsubstanz.

Als Ursache für die starke Aktivität des Säureunlöslichen kommt ein Einbau des Chalkons oder eines Abbauproduktes desselben in das Lignin nicht in Frage, da die Fixierung der Aktivität an das Säureunlösliche nicht nur in Trieben und Homogenaten, sondern auch in hitzedenaturierten Homogenaten oder in Gegenwart von Methanol/HCl erfolgt. Durch Zusatz von Rutin wurde die Fixierung merklich gehemmt, nicht aber durch Resacetophenon-4-glucosid und Phloroglucin.

Es wäre daran zu denken, dass die Fixierung durch Reaktionen zustande kommt, wie sie bei der Phloroglucin-Salzsäure-Reaktion mit Lignin ablaufen[8]. Auf jeden Fall wird durch diese noch ungeklärte Reaktion ein grosser Teil des eingesetzten Chalkons bereits in den Leitungsbahnen der Pflanze abgefangen, wodurch nur wenig Chalkon zur Biosynthese der Isoflavone in der Zelle zur Verfügung steht. Dies dürfte neben der Permeabilitätsfrage einer der Gründe sein, warum der prozentuale Einbau in die Isoflavone[3] und Flavonoide[4] relativ schlecht ist[9].

Summary. 2',4,4',6'-Tetrahydroxychalcone-2'-glucoside-[β-^{14}C] is incorporated into biochanin-A in chana germ (*Cicer arietinum* L.) without randomization of the radioactivity. Possibly a very low incorporation into formononetin occurs also. After administration of the chalcone a large part of the activity is bound to the acid insoluble residue of the cicer shoots (lignin-like substances) in an (as yet) undetermined manner. This binding also occurs in heat denatured homogenates.

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Chemisches Laboratorium der Universität Freiburg i. Br. (Deutschland), 19. Juni 1962.

[8] J. C. Pew, J. Amer. Chem. Soc. *73*, 1678 (1951).

[9] Die Arbeit wurde durch die Deutsche Forschungsgemeinschaft und den Fonds der Chemischen Industrie unterstützt.

The Condensation of Anthranilic Acid with S-Methyl-2-Thiohydantoin[1]

The condensation of aromatic amines with S-methyl-2-thiohydantoin leading to N^2-aryl-glycocyamidines gives, if applied to anthranilic acid, a product (mp.: about 340°, incorr., decomp.; found: C 59.56 H 3.70 N 20.60; $C_{10}H_7N_3O_2$ requires C 59.70 H 3.55 N 20.89) which contains 1 Mol water less than the expected glycocyamidine I[2]. This means, evidently, the formation of a third ring and thus the product may correspond to the alternative structures IIa or IIb.

Since glycocyamidines[3] and the related hydantoins and 2-thiohydantoins[4], if unsubstituted at N^1, are always acylated at N^1, structure IIa seems much more probable for the condensation product.

Structures IIa or IIb were suggested by Grout and Partridge[5] for a substance (mp.: 350°, corr.) resulting from the condensation of methyl anthranilate and ethyl N-cyanoglycinate (prepared *in situ*). By kindness of the British authors, we had the opportunity to compare both condensation products by their mp., mixed mp. (about 340°, incorr., decomp.) and IR spectra, and found them to be identical.

For the unambiguous synthesis of compound IIa we have chosen the routes a and b:

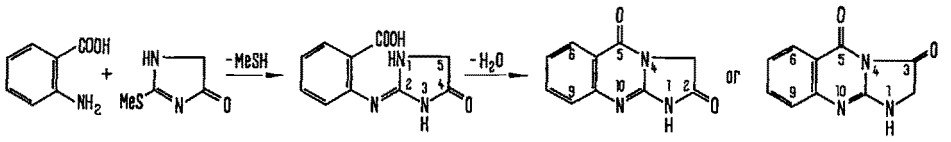
[1] Part X. Hydantoins, thiohydantoins and glycocyamidines. Part IX. K. Lempert, Chem. Ber., *95*, 1066 (1962).

[2] K. Lempert and J. Breuer, unpublished.

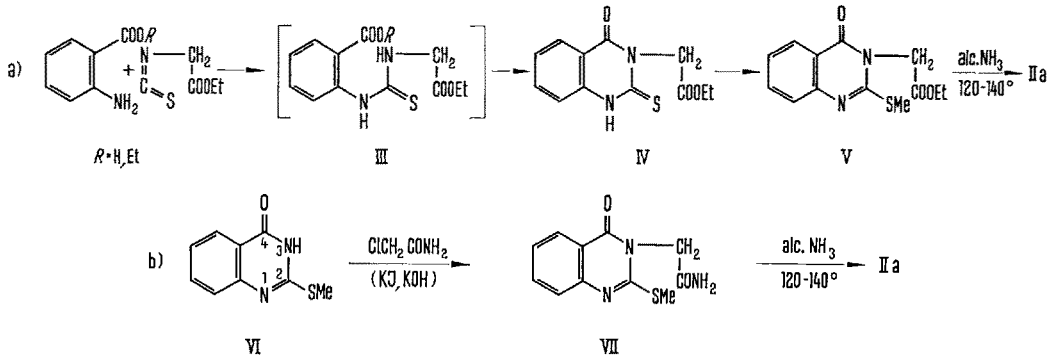
[3] Ch. Lempert, Chem. Rev. *59*, 700 (1959).

[4] E. Ware, Chem. Rev. *46*, 429 (1950).

[5] R. J. Grout and M. W. Partridge, J. chem. Soc. (London) *1960*, 3551.



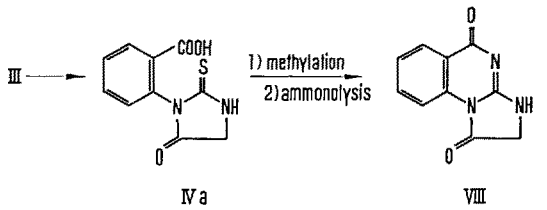
I IIa IIb



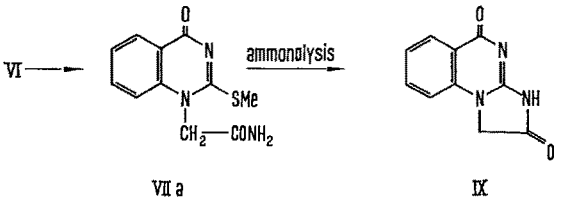
Ethyl (2-thioxo-4-oxo-1, 2, 3, 4-tetrahydro-3-quinazolinyl)-acetate (IV, mp.: 216–7°, incorr.; found: C 54.80 H 4.68 N 10.80 S 12.08; $C_{12}H_{12}N_2O_3S$ requires C 54.54 H 4.58 N 10.60 S 12.12) was prepared by refluxing either anthranilic acid or ethyl anthranilate with ethyl isothiocyanatoacetate in alcohol; methylation gave the S-methyl derivative (V, mp.: 107–8°; found: C 56.63 H 5.23 N 10.10 S 11.62; $C_{13}H_{14}N_2O_3S$ requires C 56.10 H 5.07 N 10.06 S 11.52) and ammonolysis and ring closure of the latter, effected by heating with alcoholic ammonia, led to a product (mp.: about 340°, incorr., decomp.; found: C 59.94 H 3.68 N 21.07; $C_{10}H_7N_3O_2$ requires C 59.70 H 3.55 N 20.89) which, in all respects (mp., mixed mp., IR-spectrum) proved to be identical with the condensation product from anthranilic acid and S-methyl-2-thiohydantoin.

(2-Methylmercapto-3, 4-dihydro-4-oxo-3-quinazolinyl)-acetamide (VII, mp.: 245–46°, incorr., decomp.; found: C 53.05 H 4.60 N 16.86 S 12.56; $C_{11}H_{11}N_3O_2S$ requires C 53.00 H 4.45 N 16.86 S 12.86) was prepared by reaction of 2-methylmercapto-4(3 H)-quinazolinone (VI) with chloroacetamide in the presence of potassium iodide and potassium hydroxide. Ammonolysis and ring closure was effected as above and led to a product (mp.: about 340°, incorr., decomp.; found: C 60.01 H 3.59 N 21.14; $C_{10}H_7N_3O_2$ requires C 59.70 H 3.55 N 20.89) which too proved in all respects to be identical with the products mentioned above.

Attention should be called to the fact that neither the synthesis via a nor that via b *alone* proves the structure of IIa unequivocally. Ring closure of III could lead namely, under the conditions employed, by subsequent esterification even in the case R=H instead of IV to the isomeric thiohydantoin derivative IVa which, after methylation and ammonolysis, should lead to VIII, an isomer of IIa:



VI, on the other hand, might react with chloroacetamide at N^1 instead of N^3, leading to VIIa and, after ammonolysis to IX, *another* isomer of IIa:



However, the fact that *both* syntheses give the *same* product, offers an unequivocal proof of its structure.

Thus the condensation product of anthranilic acid and S-methyl-2-thiohydantoin and that of methyl anthranilate with ethyl N-cyano-glycinate[5] has been proved to be 2,51 H, 3 H-imidazo (2,1-b) quinazolinedione (IIa).

Zusammenfassung. Die Struktur des Kondensationsproduktes aus Anthranilsäure und S-Methyl-2-thiohydantoin, bzw. aus Anthranilsäuremethylester und N-Cyanglycinäthylester[5] wurde als die eines 2,5-(1 H, 3 H) Imidazo(2,1-b) chinazolindions bewiesen.

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Steroids. The Stereochemistry of Grignard Additions to Steroidal Ketones

The addition of methyl magnesium halide to 12-pregnanones[1–3] and 17-a-*D*-homoandrostanones[4] proceed contrary to the 'rule of rear attack'[5,6]. These abnormal additions led us to survey the reactions of methyl magnesium halide and methyl lithium with steroidal ketones. It revealed the fact that in all cases recorded, the yield of axial alcohol is at least 50%. Since the analogy between the addition reaction of Grignard reagent and lithium aluminum hydride to ketones has been well authenticated[7], and as the latter reaction has been studied at greater length, a comparison of the results obtained with these

[1] G. JUST and R. NAGARAJAN, Can. J. Chem. *39*, 548 (1961).
[2] R. NAGARAJAN and G. JUST, Can. J. Chem. *39*, 1274 (1961).
[3] G. JUST and R. NAGARAJAN, Can. J. Chem. *40*, 377 (1962).
[4] L. RUZICKA, N. WAHBA, P. T. HERZIG, and H. HEUSSER, Chem. Ber. *85*, 491 (1952).
[5] L. F. FIESER, Exper. *6*, 312 (1950).
[6] T. F. GALLAGHER and T. H. KRITCHEVSKY, J. Amer. chem. Soc. *72*, 882 (1950).
[7] N. G. GAYLORD, *Reductions with Complex Metal Hydrides* (Interscience Publishers, Inc., New York 1956), p. 91 and references cited therein.