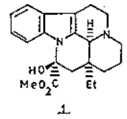

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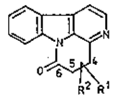
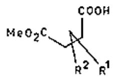
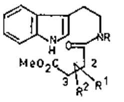


2 R^1 = 4-Et, R^2 = 4-Pr
3 R^1 = 4-Et, R^2 = 4-Me
4 R^1 = 5-Et, R^2 = 5-Pr
5 R^1 = 5-Et, R^2 = 5-Me





6 R^1 = 2-Et, R^2 = 2-Pr
7 R^1 = 2-Et, R^2 = 2-Me
8 R^1 = 3-Et, R^2 = 3-Pr
9 R^1 = 3-Et, R^2 = 3-Me

10 R^1 = 3-Et, R^2 = 3-Pr
11 R^1 = 3-Et, R^2 = 3-Me
12 R^1 = 2-Et, R^2 = 2-Pr
13 R^1 = 2-Et, R^2 = 2-Me

oder programme in this field we focused our attention on the synthesis of their degradation products — 4,5-dihydrocanthin-6-ones — particularly on (—)-4-ethyl-4-propyl-4,5-dihydro-6H-canthin-6-one 2, which was readily obtained by degradation of (+)-vincamine 1.

Starting from racemic and optically active 2,2' and 3,3-disubstituted 3-methoxycarbonylpropionic acids 6—9 the appropriate amid-esters 10—13 were prepared, which on Bischler-Napieralskii cyclization followed by selenium dehydrogenation afforded the desired 4,5-dihydrocanthin-6-ones 2—5.

The synthesis of succinic acid-esters 6—9 will be discussed briefly together with the physico-chemical properties of tryptamides 10—13 and especially of canthin-6-ones 2—5.

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LE I 18

SYNTHESIS OF SUBSTITUTED 1(2H)-ISOQUINOLINONES AND 8-OXOBERBINES FROM HOMOPHTALIC ANHYDRIDES AND AZOMETHINES

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Recently we reported that the reaction of 1,3-isochromandiones (homophtalic anhydrides) with acyclic and cyclic azomethines can be used as a method for synthesis of 4-carboxy-1(2H)-isoquinolinones, 13-carboxy-8-oxoberbines and 14-carboxy-hexadehydroyohimbanes[1,2].

Homophtalic anhydrides 1 react analogously with azomethines of aromatic, heteroaromatic and aliphatic aldehydes and ketones, and aliphatic amines 2, as well as with 1-alkyl(aryl)-6,7-dimethoxy-3,4-dihydroisoquinolines 4 (refluxing of 1 and 2, resp. 4 in benzene or dichloroethane, extraction of 3, resp. 5 with NaOH . aq), where trans-2,3-disubstituted or 2,3,3-trisubstituted-4-carboxy-3,4-dihydro-1(2H)-isoquinolinones 3 (R = H) and 14-alkyl(aryl)-13-carboxy-8-oxoberbines 5 (R = H), resp., are obtained. The relative configuration of 3 is proved chemically and by NMR-investigation of their corresponding methyl esters 3 (R = Me)[1,2]. The spatial structure of C-13 and C-14 can not be established by NMR-analysis of 5 (R = Me).

Only in the case of the reaction between 1 (R^1 = H or MeO) and ethoxymethyleneaniline (2, R^2 = H, R^3 = EtO, R^4 = Ph) 4-anilinomethylene-1,3-isochromandiones 6 (R^1 = H or MeO) are obtained. In conditions of alkaline hydrolysis they are converted into 4-carboxy-1(2H)-isoquinolinones 7 (R = H, R^1 = H or MeO, R^2 = Ph). The NMR-spectra of their methyl esters show a great similarity with the spectrum of the ester 7 (R = R^2 = Me, R^1 = H), which was obtained by us from the known acid 7 (R = H)[3]. In these two cases an aldol condensation between the CH-acidic anhydrides and the azomethine takes place.

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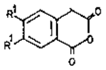

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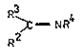

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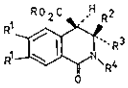
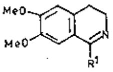
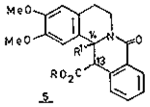


3

R = H or Me; R^1 = H or MeO; R^2 = H or Me;
R^3 = Ph, 2-furyl, Me, Et, iso-Pr etc.
R^4 = PhCH$_2$, PhCH$_2$CH$_2$, (MeO)$_2$CHCH$_2$, Me, Et, n-Pr, iso-Pr, cyclohexyl etc.

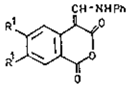


4



5

R = H or Me
R^1 = Me, Et, PhCH$_2$, Ph



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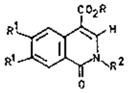

7

R = H or Me
R^1 = H or MeO
R^2 = Me or Ph

LE I 19

ON THE MECHANISM OF THE AMINATION OF 3-SUBSTITUTED DERIVATIVES OF 1,2,4-TRIAZINE WITH POTASSIUM AMIDE IN LIQUID AMMONIA

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Amination of 3-methylthio-1,2,4-triazine with potassium amide in liquid ammonia at —75 °C yields the corresponding 3-amino compound and in addition 3,3'-bis(methylthio)-5,5'-bi-1,2,4-triazine. It has been proved using the corresponding 3-methylthio-[4-^{15}N]-1,2,4-triazine that amination goes for about 93% via a ring opening - ring closure sequence (S$_N$ANRORC-mechanism)[1] (see Scheme)