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THE FORMATION OF METHYL PROPYNYLTHIENYLACRYLATE FROM DEHYDROMATRICARIA ESTER IN CHRYSANTHEMUM VULGARE

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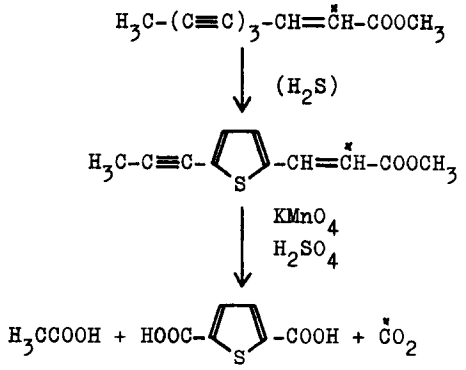
5-[Propyn-(1')-yl-(1')]-2-[2'-carbomethoxyethenyl-(1')]-thiophene which has been found in Chrysanthemum vulgare Bernh. along with dehydromatricaria ester (1) may be prepared in good yield by the addition of H_2S to the dehydromatricaria ester in weakly alkaline medium (p_H 8-10) (2). This synthesis of the alkynylthiophene is in vitro even possible, if cysteine or glutathione takes the place of H_2S in this reaction (3).We have now found that upon feeding of 2-C-14 dehydromatricaria ester to Chrysanthemum vulgare shortly before blooming there is present within 4 - 5 days in the root methyl propynylthienylacrylate in an amount of maximal 38% of that activity which is contained in those compounds being extractable by ether/ petroleum ether (1 : 1).

By oxidative degradation of the alkynylthiophene it could be shown that the marked C atom in relation to the carboxy group is in the same position as in dehydromatricaria ester; namely, in the CO_2 contents was present 95% of the activity of the alkynylthiophene. Therefore, it may be concluded that the thiophene ring closure may in vivo also take place by H_2S addition to the diyne grouping.



Apparently the plant has only shortly before blooming the possibility of forming the alkynylthiophene from the dehydromatricaria ester, because feeding experiments at an earlier stage of the vegetation period or after blooming resulted in considerably lower yields of marked thiophene.

After feeding of S-35 cysteine, we obtained an alkynylthiophene which contains 14% of that activity that is incorporated into the lipoid-soluble compounds within 3 - 4 days.

About these investigations we will report in detail at a different place.

REFERENCES

(1) E. Guddal, N.A.Sörensen, Acta Chem.Scand. 13, 1185 (1959)

(2) K.E.Schulte, J.Reisch, L.Hörner, Angew.Chem. 72, 92o (196o) und Chem.Ber. 95,1943 (1962)

(3) K.E.Schulte, J.Reisch, W.Herrmann, G.Bohn,Arch.Pharm. 296, 456 (1963)