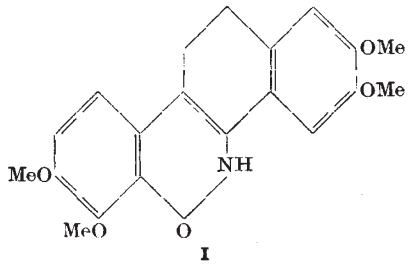
Synthesis of a Reference Compound derived from Sanguinarine and Chelerythrine

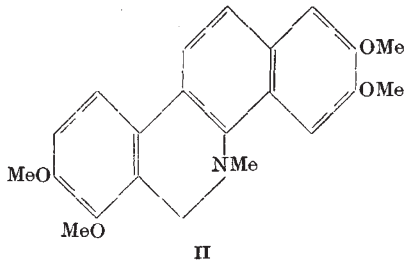
THE synthesis of 7 : 8 : 4′ : 5′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridone (I) has already been reported[1]. By treatment with phosphoryl chloride, the change —CO—NH— → —CCl=N— was readily effected (found in the product, m.p. 176–178°; C, 65·2; H, 4·9; Cl, 9·9 per cent), and this chloro-compound, in boiling *p*-cymene solution, may be reduced by hydrogen in the presence of palladized carbon and simultaneously dehydrogenated to the related tetramethoxybenzphenanthridine (—CCl=N— → —CH=N— and loss of 2H by dehydrogenation, $—CH_2.CH_2— \rightarrow —CH=CH—$) (found in the product, m.p. 217–219°; C, 71·8, 72·1; H, 5·4, 5·3; N, 3·9 per cent).

The methosulphate of the latter base was changed by double decomposition into the methochloride, melting point 207–210° (found, C, 60·3; H, 6·2; Cl, 7·6 per cent, indicating $C_{22}H_{22}O_4NCl,2H_2O$), which is the tetramethoxy-analogue of sanguinarine chloride ($2CH_2O_2$) and chelerythrine chloride ($2MeO,CH_2O_2$).

On reduction with zinc in boiling aqueous hydrochloric acid, N-methyl-7 : 8 : 4′ : 5′-tetramethoxy-9 : 10-dihydro-1 : 2-benzphenanthridine (II) was produced.



I



II

This substance was obtained by Späth and Kuffner[2] from both dihydrochelerythrine and dihydrosanguinarine by hydrolysis of methylenedioxy groups followed by methylation.

We are deeply indebted to Dr. S. N. Sarkar for a specimen of this substance which he had prepared from dihydrosanguinarine.

The synthetic specimen crystallized in colourless prisms, melting point 182–184° (slight decomp.) (found, C, 72·6, 72·7; H, 6·5, 6·1; N, 3·9 per cent), and an intimate mixture with the specimen of natural origin (m.p. 183–185°) had melting point 183–185°.

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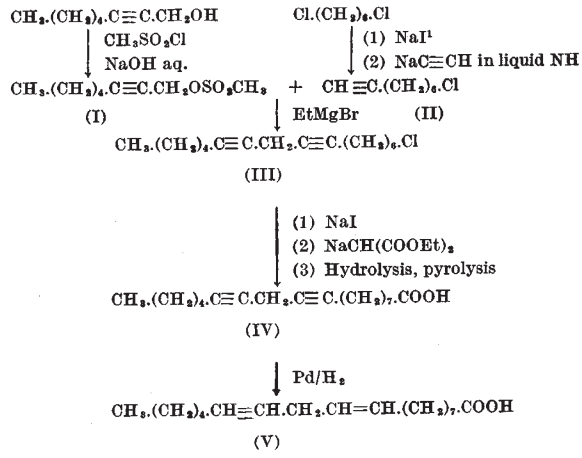
[1] Bailey and Robinson, *Nature*, **164**, 402 (1949).
[2] Späth and Kuffner, *Ber. deut. chem. Ges.*, **64**, 2034 (1931).

Synthesis of Linoleic Acid

THE problem of the synthesis of the naturally occurring unsaturated aliphatic acids (nearly all of which possess the *cis* configuration about the double bonds) has only recently come under investigation in any detail. This is mainly due to the difficulty of obtaining, by classical methods, pure *cis*-ethylenic compounds. The present rapid development of acetylene chemistry, coupled with the fact that catalytic partial hydrogenation of the triple bond results in the formation of an ethylenic compound of *cis* configuration, has removed this stumbling-block, and the exploitation of this technique is being widely studied.

The recent work of Ahmad, Bumpus and Strong[1] has established an elegant method of striking simplicity for producing long-chain monoacetylenic acids of type $CH_3.(CH_2)_x.C\equiv C.(CH_2)_y.COOH$ and thence, by catalytic partial hydrogenation, the corresponding *cis*-ethylenic acids. At the moment, this certainly constitutes the best procedure for synthesizing the natural mono-ethylenic fatty acids (for example, oleic acid, erucic acid, etc.).

A great many of the natural polyethylenic acids contain the grouping *cis* : *cis*— $CH=CH.CH_2.CH=CH$—. One of the most important of these is the widely distributed linoleic acid (octadeca-9 : 12-dienoic acid) (V), the characteristic acid constituent of the semi-drying oils[2]; the substance has added interest by virtue of its properties as an essential food factor[3]. The obvious intermediate for the synthesis of this compound is the corresponding β-diacetylenic acid (IV). A review of the scanty literature on β-diacetylenes reveals the inaccessibility of these compounds; only a few hydrocarbons of this series have been obtained, and these in poor yield owing to the reactivity of the methylene group situated between the triple bonds[4].



We have been successful in obtaining the required β-diacetylenic acid intermediate (IV) by the route indicated. An ethereal solution of the Grignard complex of the acetylenic chloride (II) was very slowly added to a boiling ethereal solution of an excess of the acetylenic methanesulphonate (I). This condensation procedure ensured that no excess Grignard reagent was present at any time to attack the central methylene group of the product (III). Conversion of the latter to the iodide, followed by the familiar malonic ester chain-lengthening process, yielded the