residue from acetone 215 mg. of XIII, m.p. 245–247°, were obtained, $[\alpha]_D^{25} + 130°$ (c 0.75 in chloroform; $\alpha + 0.98°$) λ_{max}^{ether} 243 mμ (ϵ 10,700); λ_{max}^{Nujol} 5.67 μ, 5.78 μ.

Anal. Calcd. for $C_{23}H_{28}O_4Se$: C, 61.74; H, 6.31. Found: C, 62.00; H, 6.53.

Deacetylation of XIII *to* XIV. A total of 200 mg. of XIII was refluxed in 30 ml. of 2% methanolic potassium hydroxide for 75 min. The reaction mixture was neutralized with 1 ml. of acetic acid, diluted with chloroform, washed with water, and concentrated to dryness *in vacuo*. From acetone 81 mg. of yellow crystals of XIV, m.p. 209–211°, were obtained. By repeated recrystallization from acetone the melting point was raised to 213–214°C. $[\alpha]_D^{23} + 638°$ (c 0.58 in chloroform; $\alpha + 3.68°$) λ_{max}^{alc} 258 mμ (ϵ 5200); 292 mμ (ϵ 3500); 325 mμ (shoulder) (ϵ 2700) λ_{max} (ethanolic KOH): 314 mμ (ϵ 6950); λ_{max}^{Nujol} 2.96 μ (hydroxyl) 6.35 μ, 6.41 μ.

Anal. Calcd. for $C_{19}H_{24}O_2Se$: C, 62.80; H, 6.66; Se, 21.73. Found: C, 62.58; H, 7.25; Se, 21.28.

$\Delta^{1,4}$-*Cholestadiene-3-one* (IV) *from seleno-*$\Delta^{1,4}$*-cholestadiene-3-one* (*VII*). To 200 mg. of VII in 15 ml. of benzene there was added 3 g. of Raney nickel in 6 ml. of ethanol. The mixture was refluxed for 5 hr., filtered from nickel, washed with water, and concentrated to dryness *in vacuo*. The colorless residue (178 mg.) was chromatographed on alumina. Fractions obtained with hexane-benzene solvent mixtures in order of elution were: (a) crystalline mixtures, m.p. range 40–55°C., of Δ^4-cholesten-3-one, cholestan-3-one, and/or coprostan-3-one. These mixtures exhibited ultraviolet maxima at 240 mμ (ϵ 3000) and an infrared band at 5.82 μ (3-keto). They were not further purified; (b) several crystalline fractions, m.p. range 88–95°, which upon recrystallization from methanol yielded 25 mg. of IV, m.p. 108–110°, $[\alpha]_D^{28} + 29.3°$ (c 0.82 in chloroform), λ_{max}^{EtOH} 244 mμ, (ϵ 12,500), λ_{max}^{Nujol} 6.01 μ, 6.15 μ, 6.24 μ ($\Delta^{1,4}$-3-keto).

Anal. Calcd. for $C_{27}H_{42}O$: C, 84.75; H, 11.07. Found: C, 84.62; H, 10.92.

Pyrolysis of seleno-$\Delta^{1,4}$*-cholestadiene-3-one* (VII). A total of 500 mg. of VII was heated to 350–370°C. at 1 mm. pressure for 30 min. The odor of H_2Se was detected. The reaction mixture was diluted with chloroform, filtered from 65 mg. of metallic selenium (77% of theory), washed with water, and concentrated to dryness *in vacuo*. The residue was chromatographed on alumina. With hexane-benzene solvent mixtures several crystalline fractions, totalling 150 mg., m.p. range 65–75°C., were eluted. All fractions exhibited ultraviolet maxima at 240 mμ and 280 mμ (in ethanol) of varying intensity. In the earlier fractions the 240 mμ maximum, in the later fractions the 284 mμ maximum, was the stronger. Repeated recrystallizations of various fractions did not yield material exhibiting one or the other maximum exclusively.

Hydrogen peroxide oxidation of seleno-1-dehydro-testosterone acetate (VIII) *to selenoxide* XVIII *at room temperature.* To 100 mg. of VIII in 1 ml. of acetic acid was added 0.15 ml. of 50% hydrogen peroxide. The solution was kept at room temperature for 20 min. and then diluted with water until precipitation occurred. The precipitate was collected and upon crystallization from acetone yielded 43 mg. of crystalline XVIII, m.p. 150–155°. By recrystallization from acetone the melting point was raised to 155–157° (with some dec.); $[\alpha]_D^{23} - 44°$ (c 0.51 in chloroform; $\alpha - 0.22°$) λ_{max}^{alc} 248 mμ (ϵ 11,500); λ_{max}^{Nujol} 5.76 μ; 6.02 μ, 6.14 μ, 6.23 μ.

Anal. Calcd. for $C_{21}H_{28}O_5Se$: C, 57.40; H, 6.42; Se, 17.97. Found: C, 57.72; H, 6.50; Se, 21.91.

A solution of 40 mg. of XVIII in 10 ml. of ethyl acetate was shaken with a 10% aqueous solution of sodium bisulfite. Upon evaporation of the solvent 32 mg. of VIII, m.p. 148–152°, were isolated.

Acknowledgment. The authors wish to thank Dr. J. Fried for many stimulating discussions and suggestions. They are indebted also to Mr. J. Alicino and his associates for the microanalyses and to Dr. Nettie H. Coy and her colleagues, Mr. C. Sabo, and Mr. Charles Fairchild, for the infrared and ultra-violet measurements.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, ABERDEEN]

Flavothebaone. Part II. Exhaustive Methylation of Flavothebaone Trimethyl Ether[1,2]

K. W. BENTLEY, J. DOMINGUEZ, AND J. P. RINGE

Received September 21, 1956

Flavothebaone trimethyl ether methine ($C_{28}H_{31}O_5N$), on heating with alcoholic potassium hydroxide suffers molecular rearrangement to a *pseudo*methine ($C_{27}H_{33}O_5N$), acetolysis, and further Hofmann degradation of which affords derivatives of 1,2,7,10-tetramethoxychrysofluorene. On the basis of these results and of spectral data a complete structure is allotted to the *pseudo*methine.

In part I of this investigation,[3] flavothebaone trimethyl ether methine was shown to contain an aromatization-blocking group, presumably the quinol dimethyl ether nucleus at C_{14} of the phenanthrene skeleton, and the part-structure (I) was allotted to flavothebaone. Further confirmation of the presence of the substituent at C_{14} is provided by the fact that the 7,8-double bond in the trimethyl ether methine does not migrate into conjugation with that at position 9,10- when the methine is heated with alcoholic potash (contrast the behavior of α-codeimethine [II][4] and $\Delta^{7,9}$-thebainone methine [III][5]. Under these conditions

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[1] An account of part of the work of J. Dominguez (D. Phil. thesis, Oxford, 1953) and J. P. Ringe (Ph.D. thesis, Aberdeen, August 1956).

[2] K. W. Bentley, J. Dominguez, and J. P. Ringe, *Chemistry and Industry*, 1353 (1956).

[3] K. W. Bentley and J. Dominguez, *J. Org. Chem.*, 21, 1348 (1956).

[4] L. Knorr and S. Smiles, *Ber.*, **35**, 3009 (1902).

[5] K. W. Bentley and H. M. E. Cardwell, *J. Chem. Soc.*, 3245 (1955).

the trimethyl ether methine, $C_{28}H_{31}O_5N$, which contains no C—CH_3 group, is converted into a *pseudo*methine, $C_{27}H_{33}O_5N$, which contains one C—CH_3 group and one *saturated* carbonyl group (infrared band at 5.83 μ, 1717 cm.$^{-1}$). The ultraviolet spectrum of this base (Fig. 1) is styrenoid, but is different from those of the methine and α-codeimethine (II), from which we may conclude that the double bond is conjugated with the quinol dimethyl ether rather than the veratrole nucleus. This double bond must be heavily substituted or otherwise sterically hindered as reduction of the ψ-methine cannot be effected catalytically or with sodium amalgam. Reduction can be accomplished with sodium, liquid ammonia, and 2-ethoxyethanol, but several changes occur and these are discussed later. The ψ-methine contains a reactive methylene group and condenses with piperonal to give a piperonylidene derivative (ultraviolet spectrum Fig. 1; carbonyl absorption band 5.97 μ, 1675 cm.$^{-1}$), and this piperonylidene derivative contains no C—CH_3 group, indicating that the ψ-methine itself contains the system —CO—CH_3. In contrast to the ψ-methine the methine cannot be condensed with piperonal.

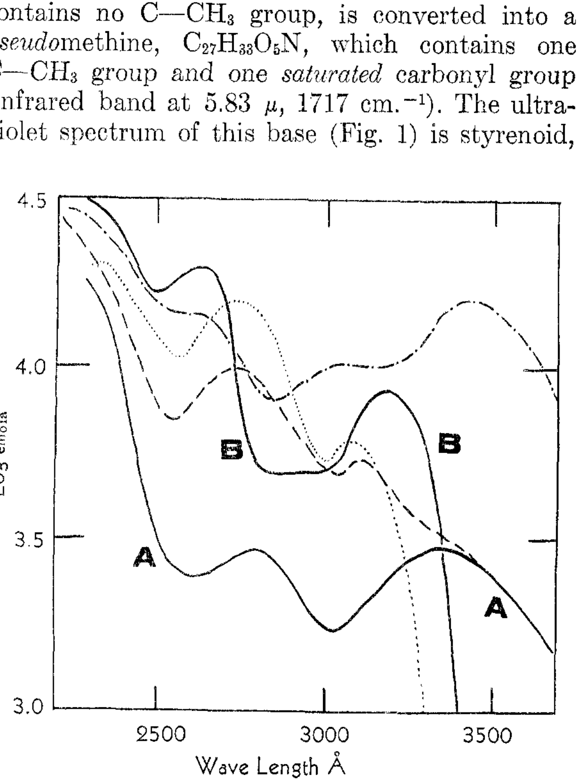

FIG. 1. ——— (A) Flavothebaone trimethyl ether; ——— (B) Flavothebaone trimethyl ether ψ-methine; – – – – – Flavothebaone trimethyl ether methine; . . . . . α-Codeimethine; – · – · – Piperonylidene flavothebaone trimethyl ether ψ-methine.

That aromatization is no longer blocked in the ψ-methine is demonstrated by the fact that the acetolysis of the methiodide affords an optically inactive aromatic substance (Compound B), $C_{23}H_{22}O_5$. The same substance together with Compound C ($C_{22}H_{22}O_4$) and Compound D ($C_{21}H_{20}O_4$) and undegraded base, was obtained by the dry-distillation of the ψ-methine methohydroxide. These three nitrogen-free products were also obtained by the dry-distillation of flavothebaone trimethyl ether methine methohydroxide; doubtless prior conversion to the ψ-methine methohydroxide occurs under the strongly alkaline conditions of this reaction, a view supported by the fact that the base recovered from the products of degradation was found to be the ψ-methine.

Compounds B, C, and D (the compositions of which are supported by molecular weights determined by the crystallographic method) are all optically inactive, and all have the same characteristic ultraviolet spectrum (Fig. 2), which is very similar to those of β- but not α-phenylnaphthalenes[6] and in accord with such an aromatic formulation all three compounds form complexes with 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, and picric acid. The simplest of these compounds, Compound D $C_{21}H_{20}O_4$, has one carbon atom more than a tetramethoxy-β-phenylnaphthalene, $C_{20}H_{20}O_4$, and the only logical formula for this substance is that of a tetramethoxybenzofluorene. Comparison of the spectra of Compound D and the three benzofluorenes[7] and allowing for the fact that methoxyl groups decrease the intensity of strong bands and increase the itensity of weak bands, thus effecting a general smoothing out of the spectra, there is a strong similarity between the spectrum of Compound D and those of 1,2- and 2,3-benzofluorene.

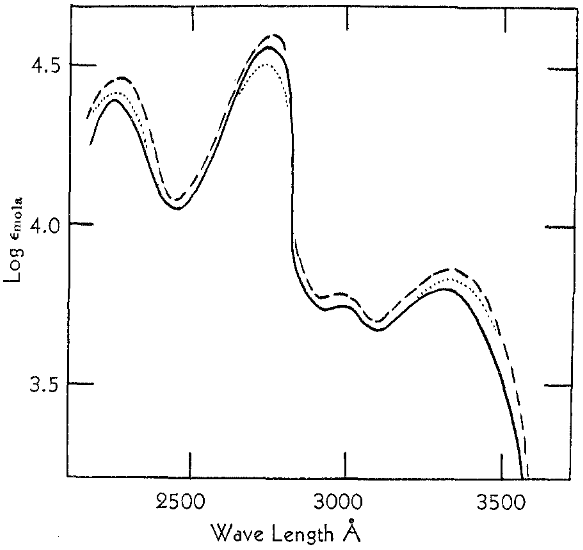

FIG. 2. ——— Compound D; – – – – – Compound C; . . . . . Compound B.

If the quinol dimethyl ether nucleus at C_{14} in flavothebaone trimethyl ether methine is assumed to retain that position throughout the degradations leading to Compound D only two structures need be considered for this substance, namely (IV, R = H) and (V, R = H). Compound B, $C_{23}H_{22}O_5$, can

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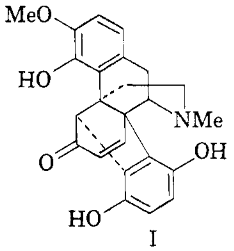
[6] R. A. Friedel, M. Orchin, and L. Reggel, *J. Am. Chem. Soc.*, **70**, 199 (1948).

[7] M. Orchin and R. A. Friedel, *J. Am. Chem. Soc.*, **71**, 3002 (1949).

be converted into Compound D, $C_{21}H_{20}O_4$, by heating with alkalis, during which process one molecular equivalent of acetic acid is liberated; Compound B can thus be allotted the structure (IV, R = $COCH_3$) or (V, R = $COCH_3$) and the hydrolysis of a 9-acetylfluorene in alkalis is unexceptional.

Compound C has been shown to be methyl-D *i.e.* (IV, R = Me) or (V, R = Me) since it is obtained when Compound D is heated with sodium methoxide and anhydrous methanol, following the method of Schoen and Becker.[8] Compound C does not give acetic acid on oxidation by the Kuhn-Roth procedure, presumably because it is oxidized to formic acid and the fluorenone. We have been unable to introduce groups larger than CH_3 into Compound D, and an attempt to prepare Compound B by the action of potassium ethoxide and ethyl acetate on Compound D afforded only the corresponding fluorenone, which doubtless arises by air oxidation of the intermediate carbanion. The carbonyl absorption band of this substance is at 1703 cm.$^{-1}$ and this may be compared with 1702, 1718, and 1712 cm.$^{-1}$ given by Bergmann and Pinchas[9] for the 1,2,-2,3-, and 3,4-benzofluorenones, and 1709, 1712, and 1719 cm.$^{-1}$ given by Josien and Fuson[10] for the same three compounds; Compounds B, C, and D may thus with confidence be formulated as derivatives of 1,2-benzofluorene.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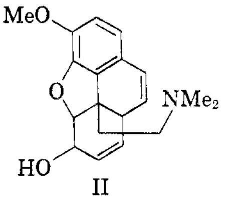
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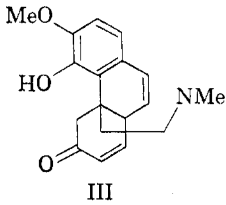
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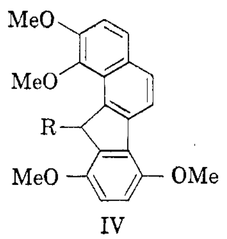
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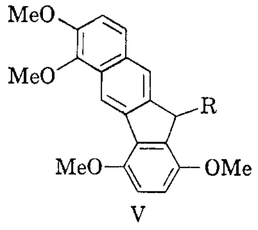
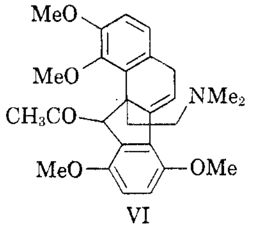
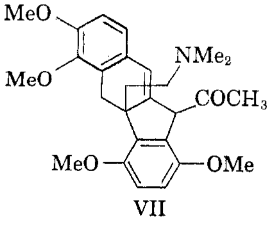
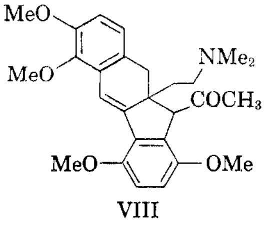

V


VI


VII


VIII

These results allow a virtually unambiguous assignment of structure to flavothebaone trimethyl ether ψ-methine. As in other cases in the morphine-thebaine group of alkaloids the extrusion of the nitrogen-containing side-chain during the acetolysis of the ψ-methine methiodide indicates that this chain occupies an angular position, and the structure (VI) can be confidently adopted for this base. The alternative structure (VII) contains an α-codeimethine chromophore and would also be expected to undergo transformation into an α,β-unsaturated ketone under the strongly alkaline conditions of the conversion of the methine into the ψ-methine, and the structure (VIII) contains a stilbene system.

The placing of the double bond as shown in (VI) is supported by the resistance of the ψ-methine to hydrogenation, by the ultraviolet spectrum (Fig. 1), and by the presence in the infrared spectrum of the ψ-methine and in the spectra of its derivatives of an absorption band at about 12.15 μ (820–825 cm.$^{-1}$) that is not present in the spectra of other derivatives of flavothebaone. This band is however present in the spectra of fourteen other derivatives of thebaine containing a trisubstituted double bond, and is attributed to the out of plane hydrogen bending of C=CH—.

With the allocation of the structure (VI) to the ψ-methine the compounds B, C, and D are seen to be 11-acetyl-1,2,7,10-tetramethoxychrysofluorene (IV, R = Ac), 11-methyl-1,2,7,10-tetramethoxychrysofluorene (IV, R = CH_3), and 1,2,7,10-tetramethoxychrysofluorene (IV, R = H), respectively.

The primary product of the degradation of the ψ-methine methohydroxide is presumably the acetyl compound (IV, R = $COCH_3$), and this is in part hydrolyzed under the alkaline conditions to (IV, R = H), which is the sole nitrogen-free product if the methine or ψ-methine methiodide is heated with sodium cyclohexyloxide in boiling cyclohexanol. If, however, this reaction is modified and the methine or ψ-methine quaternary salt is heated with potassium hydroxide in cyclohexanol the formation of Compound D is accompanied by the production of an optically active substance, Compound E.

Compound E has the composition $C_{25}H_{26}O_5$, contains an unreducible styrenoid or stilbenoid chromophore and an α,β-unsaturated ketone system (infrared band at 5.99 μ, 1670 cm.$^{-1}$), and may be reduced to a dihydro derivative $C_{25}H_{28}O_5$ that still contains these two systems (carbonyl band at 5.99 μ, 1670 cm.$^{-1}$). The transformation of the ψ-meth-

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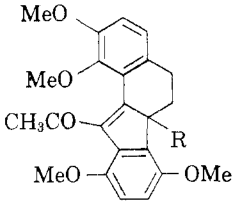
[8] K. L. Schoen and E. I. Becker, *J. Am. Chem. Soc.*, **77**, 6030 (1955).

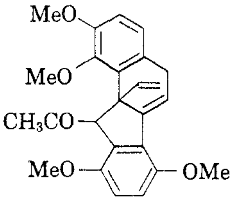
[9] E. D. Bergmann and S. Pinchas, *J. Chim. Phys.*, **49**, 537 (1952).

[10] M. L. Josien and N. Fuson, *Compt. Rend.*, **236**, 1879 (1953).

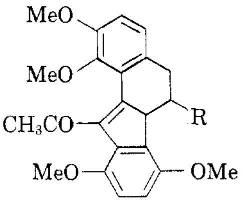
ine into Compound E is accompanied by an inversion of the sign of optical rotation ($[\alpha]_D$ changes from $+185.5°$ to $-292.5°$) and such a large change suggests that one or more centers of dissymmetry have been modified. Reduction of Compound E results in a change of $[\alpha]_D$ from $-292.5°$ to $-67.8°$ indicating that reduction of a double bond α,β to a center of dissymmetry has been effected. Compound E is not the simple product of exhaustive methylation of the ψ-methine, *i.e.*, the vinyl compound (IX), which has been obtained in a different way[11] and has the same sign of rotation ($[\alpha]_D$ $+142°$) as the parent base. These facts, coupled with our failure to convert Compound E into B, C, or D, suggest the structure (X, R = $CH{=}CH_2$) for this substance, and the structure (X, R = Et) for its dihydro-derivative;[12] the fully substituted double bond would be expected to resist catalytic hydrogenation.



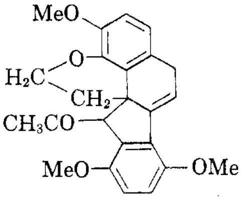
Xa



IX



X



XI

A very small amount of yet another nitrogen-free product was obtained during the dry-distillation of the ψ-methine methohydroxide. This substance (which we have called Compound F) is optically active, has the composition $C_{24}H_{24}O_5$, contains one $C{-}CH_3$ group and only three methoxyl groups, has a styrenoid ultraviolet spectrum, and is a saturated ketone (infrared bands at 5.84 μ, 1720 cm.$^{-1}$). An insufficient amount of this material was obtained to permit further examination, but we believe that Compound F has the structure (XI). (It has been shown that the tendency to form the thebenone type of cyclic ether system during the dry-distillation of methohydroxides in the morphine group is so strong that a methoxyl group at position 4 may suffer demethylation.[13])

Satisfactory mechanisms may be advanced for the production of all of the above nitrogen-free products from the ψ-methine methohydroxide as follows.

(a) A proton is extracted from the ψ-methine salt as shown in (XII), and the resulting carbanion eliminates ethylene and trimethylamine by the concerted process shown in (XII) → (XIV), finally giving Compound B (XV).

(b) Hydrolysis of a portion of Compound B affords Compound D (XVI).

(c) At the same time some of the methohydroxide loses methanol, giving the ψ-methine base, which is recovered from the products of the degradation.

(d) The methanol so formed effects a base-catalyzed methylation of Compound D to Compound C (XVIII) via the intermediate (XVII): Compound C could also arise from Compound B via the methylol (XVa) which would suffer cleavage in base as shown in (XVb) → (XVII). As expected on the basis of either of these processes no methyl-B was isolated from the products of degradation.

(e) Trimethylamine could be eliminated from the carbanion resulting from the proton extraction shown in (XII) by an alternative process shown in (XIX); the product (XX) could be further degraded by alkali to give the β,γ-unsaturated ketone (XXI), which through the enol would be readily transformed into the α,β-unsaturated ketone Compound E (XXII). The only other reasonable product of alkaline degradation of the ketone (XX) would be the vinyl compound (IX). It may be stated at this point that the reaction mixture in the degradations in cyclohexanol leading to Compound E rapidly becomes dark orange in color and then slowly fades to a pale straw yellow.

(f) The production of Compound B by the acetolysis of the ψ-methine methiodide presumably proceeds by the process (XII) → (XIV) with $OAc^{\ominus}$ as the attacking ion, and the production of the thebenone type of compound, Compound F, presumably involves the processes shown in (XXIII) → (XI).

As stated above, the reduction of the ψ-methine with sodium in liquid ammonia is complex. In order to keep the ψ-methine partly in solution in the ammonia the reduction had to be carried out in the presence of 2-ethoxyethanol, which also acted as proton source. The primary reduction product

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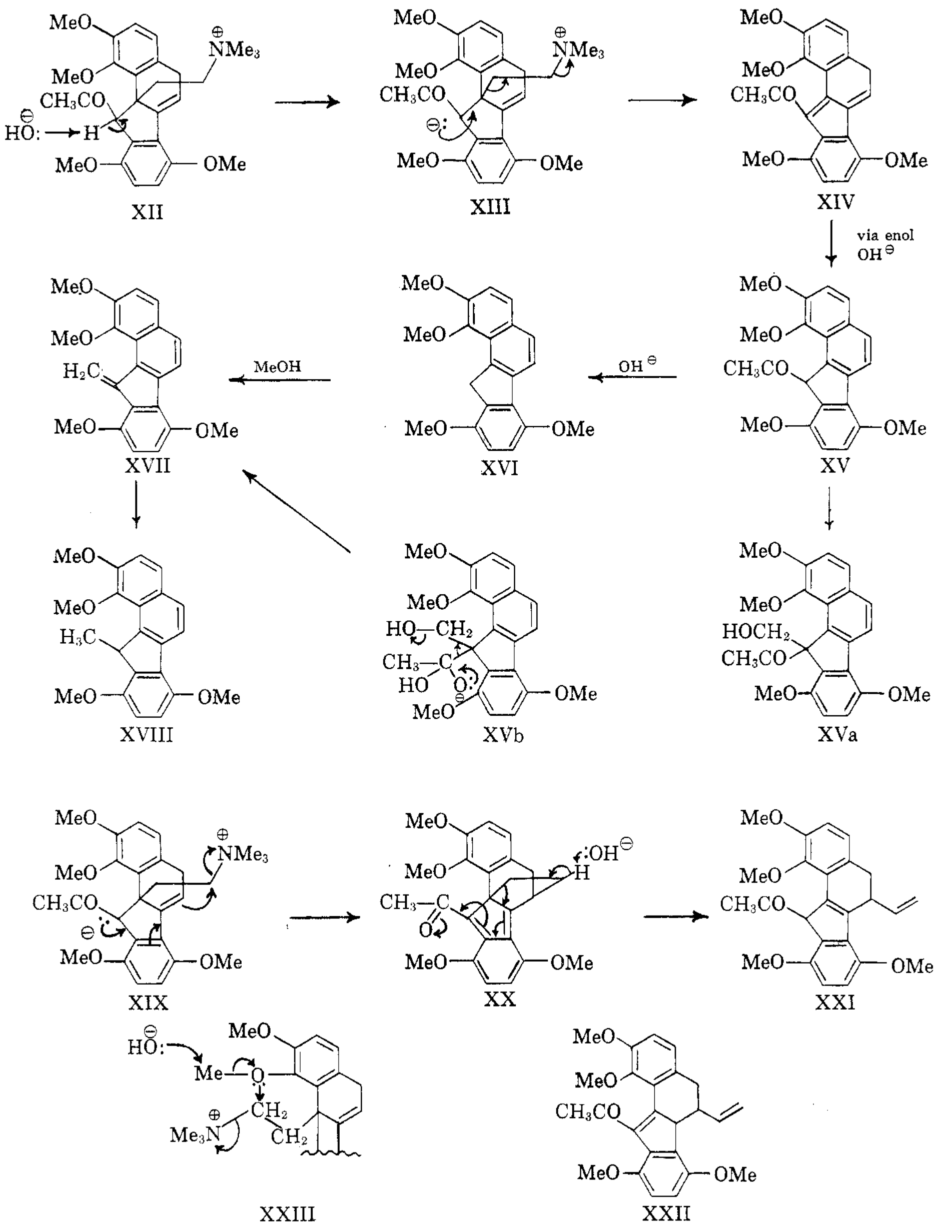
(11) K. W. Bentley, J. Dominguez, and J. P. Ringe, Part IV of this series, *J. Org. Chem.*, **22**, 422 (1957).

(12) Compound E and Dihydro-Compound E were originally allotted the structures (Xa, R = $CH{=}CH_2$) and (Xa, R = Et) respectively (ref. 2 above). These structures are equally in accord with the chemical facts, but no rational mechanism for the production of such compounds from the ψ-methine can be advanced.

(13) L. J. Sargent and L. F. Small, *J. Org. Chem.*, **16**, 1031 (1951).



was presumably more soluble in the mixture than the starting material, and readily underwent further reduction. The ultraviolet spectrum of the product showed that the styrenoid double bond of the ψ-methine had been reduced, and the infrared spectrum showed no carbonyl bands; no reducible double bond was found to be present; the analytical data for the base, the perchlorate and the picrate all indicated the composition $C_{26}H_{35}O_3N$ for the base. This composition suggested that the base had lost one methoxyl group, and this was confirmed by analyses of two further degradation products (see below). The reduction of the styrenoid double bond is unexceptional and the reduction of the carbonyl group to —CH_2— doubtless proceeds via the secondary alcohol followed by base-catalyzed dehydration and reduction of the resulting styrene, but the removal of a methoxyl group is not so common; usually the aromatic nucleus is reduced to a dihydro-compound. Birch has shown that in reductions with sodium, ammonia, and an alcohol the ammonia functions only as a solvent, that the process is anionoid and proceeds by the α,δ-addition of electrons across the benzene ring.[14] He has shown that the reduction will tend to be initiated (a) in an unoccupied position and (b) *ortho* or *meta* rather than *para* to an alkyl group. Thus in the ψ-methine (XXIV) the methoxyl group at position 1 is most likely to be lost since the position opposite C_2 is occupied by a carbon atom and the positions opposite both C_7 and C_{10} are occupied by methoxyl groups. The reduction may therefore be represented as shown in (XXIV) → (XXV) → (XXVI), the last of these structures be-

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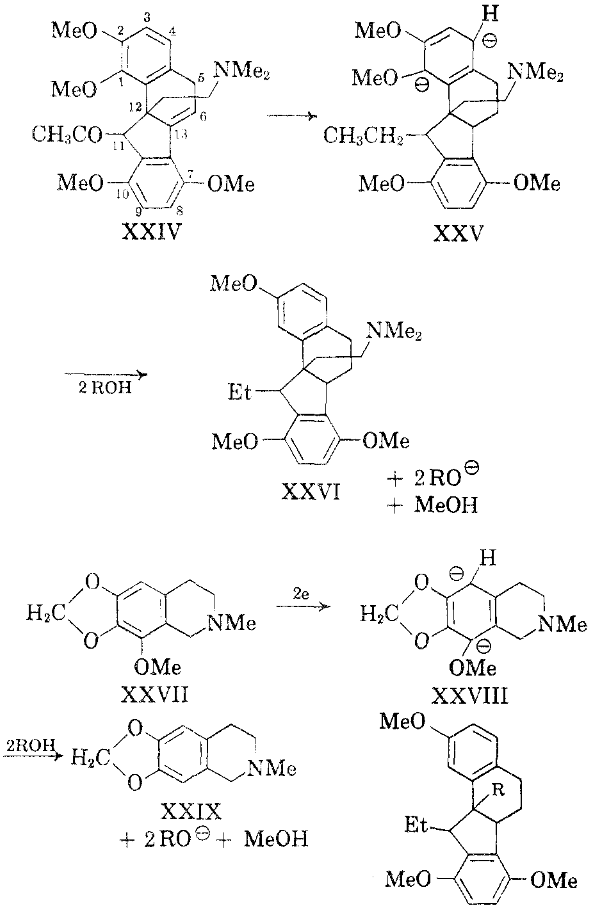
[14] A. J. Birch, *J. Chem. Soc.*, 430 (1944).

ing that of the final reduction product, which is thus 12-β-dimethylaminoethyl-11-ethyl-2,7,10-trimethoxy-5,6,12,13-tetrahydrochrysofluorene. The removal of the methoxyl group may be likened to the removal of such a group during the reduction of hydrocotarnine to hydrohydrastinine (XXVII) → (XXIX) by sodium and an alcohol in toluene.[15]



Degradation of this new base (which may be named flavothebaone trimethyl ether desmethoxydesoxodihydro-ψ-methine) *via* the *N*-oxide following the method of Bentley, Ball, and Ringe,[16] afforded the corresponding desaza compound (XXX, R = CH=CH$_2$) which was reduced to the dihydrodesaza compound (XXX, R = Et). The analytical data for these two new compounds confirmed that one methoxyl group was lost during the reduction of the ψ-methine.

EXPERIMENTAL

Flavothebaone trimethyl ether ψ-methine. A mixture of flavothebaone trimethyl ether methine (35 g.) and a 25% solution of potassium hydroxide in 50% ethanol (600 ml.) was boiled for 6 hr. under reflux, with vigorous stirring, and allowed to cool to room temperature. The crystalline solid was collected and recrystallized from 50% ethanol, when the ψ-methine was obtained as colorless irregular prisms, m.p. 187°, $[\alpha]^{20}_{D}$ +185.5° (CHCl$_3$, c 1.7), yield 2.9 g.

Anal. Calcd. for $C_{27}H_{33}O_5N$: C, 71.7; H, 7.3; Mol. Wt., 451. Found: C, 71.5, 71.8; H, 7.2, 7.3; Mol. Wt. (crystallographic) 440 ± 8.

The *perchlorate,* prepared in and recrystallized from 90% ethanol, was obtained as colorless prisms, m.p. 151°, $[\alpha]^{18}_{D}$ +172.5 (EtOH, c 0.5).

Anal. Calcd. for $C_{27}H_{33}O_5N \cdot HClO_4 \cdot H_2O$: C, 56.8; H, 6.3. Found: C, 56.5; H, 6.5.

The *picrate,* prepared in ethanol and recrystallized from 2-ethoxyethanol, was obtained as canary yellow plates, m.p. 219°.

Anal. Calcd. for $C_{27}H_{33}O_5N \cdot C_6H_3O_7N_3$: C, 58.2; H, 5.3. Found: C, 58.5; H, 5.6.

The *methiodide,* prepared in benzene and recrystallized from water, was obtained as colorless prisms, m.p. 176°.

Anal. Calcd. for $C_{27}H_{33}O_5N \cdot CH_3I \cdot H_2O$: C, 35.0; H, 6.2; I, 20.7. Found: C, 54.8; H, 6.1; I, 20.9.

The *methoperchlorate,* obtained from the methiodide and sodium perchlorate, was recrystallized from 50% ethanol, when it was obtained as colorless irregular prisms, m.p. 178°, $[\alpha]^{22}_{D}$ +176° (50% EtOH, c 1.5).

Anal. Calcd. for $C_{27}H_{33}O_5N \cdot CH_3ClO_4$: C, 59.2; H, 6.4; Cl 6.3. Found: C, 59.2; H, 6.7; Cl, 6.8.

The *oxime* was prepared by heating a mixture of the base (1 g.), hydroxylamine hydrochloride (1 g.) and water (50 ml.) under reflux for 3 hr., cooling, and neutralizing with aqueous sodium carbonate. It was obtained as colorless prisms, m.p. 227–228°, $[\alpha]^{18}_{D}$ +256° (EtOH, c 1.1), on recrystallization from 50% ethanol.

Anal. Calcd. for $C_{27}H_{34}O_5N_2$: C, 68.8; H, 7.7. Found: C, 69.1; H, 7.6.

The *piperonylidene* derivative was prepared by heating the ψ-methine (0.8 g.), piperonal (0.8 g.), and a solution of sodium (0.1 g.) in ethanol (17 ml.) under reflux for 4 hr., during which time the mixture became red. The ethanol was removed *in vacuo,* the residue shaken with 1*N* hydrochloric acid (10 ml.) and ether (10 ml.), the aqueous layer separated and neutralized with ammonia. The precipitated base was extracted with ether, and was finally obtained as a yellow amorphous solid, $[\alpha]^{18.5}_{D}$ +307° (CHCl$_3$, c 2.12), carbonyl absorption band 5.95μ.

Anal. Calcd. for $C_{35}H_{37}O_7N$: C, 71.9; H, 6.3. Found, C, 71.5; H, 6.7.

Attempted reduction of flavothebaone trimethyl ether ψ-methine. The ψ-methine was recovered unchanged after hydrogenation over platinum oxide in glacial acetic acid at 150°/18–28 atm., and in the presence of concentrated hydrochloric acid at temperatures up to 90°. It was also recovered unchanged after treatment with 3% sodium amalgam in boiling ethanol and in dilute acetic acid, and after standing with sodium borohydride in ethanol and in pyridine for 24 hr. Attempts to reduce the carbonyl group by Huang-Minlon's method yielded intractable phenolic bases. For reduction with sodium and liquid ammonia see below.

Acetolysis of flavothebaone trimethyl ether ψ-methine methiodide. The ψ-methine methiodide (3.97 g.), anhydrous sodium acetate (1.08 g.), and acetic anhydride (60 ml.) were boiled together under reflux for 1 hr., silver acetate (1.07 g.) was added and the mixture boiled for a further 4 hr. The precipitated silver iodide was removed by filtration, and the filtrate heated in sealed tubes at 180–190° for 48 hr. During the opening of the tubes agitation was carefully avoided, otherwise violent evolution of a volatile substance occurred and much material was lost. The dark liquid was filtered from a small amount of carbonized material, the acetic anhydride removed *in vacuo* and the residue extracted with benzene. The benzene extract was shaken with 2*N* hydrochloric acid, washed with water, and dried; on evaporation it afforded the *neutral fraction.* A *basic fraction* was recovered from the hydrochloric acid washings by neutralization with

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(15) D. B. Clayson, *J. Chem. Soc.,* 2016 (1949).

(16) K. W. Bentley, J. C. Ball, and J. P. Ringe, *J. Chem. Soc.,* 1963 (1956).

ammonia and extraction with ether. These two fractions were further examined as follows.

The basic fraction. After removal of the solvent the residue was recrystallized from 50% ethanol, when it was obtained as light brown prisms m.p. 174–177°, raised to 185° on further crystallization. This material was identified with the ψ-methine.

The neutral fraction. This was obtained as a dark tan on evaporation of the benzene solution. It was dissolved in benzene (100 ml.) and sufficient light petroleum (b.p. 50–60°) added to produce a slight turbidity. The resulting solution was chromatographed on alumina, and a yellow-orange band so obtained eluted with a 1:1 mixture of benzene and light petroleum (b.p. 50–60°). Evaporation of the eluate afforded a reddish oil, which, on trituration with ethanol gave 0.32 g. of yellow crystalline material, m.p. 175–177°. Recrystallization of this material yielded Compound B, *11-acetyl-1,2,7,10-tetramethoxychrysofluorene* as yellow prisms, m.p. 178°, $[\alpha]^{20}_{D}$ 0.0 (EtOH, $CHCl_3$).

Anal. Calcd. for $C_{23}H_{22}O_5$: C, 73.0; H, 5.8; OMe, 32.8; CH_3CO, 11.4. Found: C, 72.6; H, 5.9; OMe, 33.5; CH_3CO, 11.9.

The *1,3,5-trinitrobenzene complex* was prepared in ethanol and recrystallized from light petroleum (b.p. 100–120°), when it was obtained as red needles, m.p. 147–148°.

Anal. Calcd. for $C_{23}H_{22}O_5 \cdot C_6H_3O_6N_3$: C, 59.0; H, 4.2; N, 7.1. Found: C, 59.2; H, 4.4; N, 7.3.

The *picrate*, prepared in ethanol, was obtained as dark brown irregular prisms, m.p. 131–132°. It could only be recrystallized from ethanol in the presence of excess of picric acid.

Anal. Calcd. for $C_{22}H_{23}O_5 \cdot C_6H_3O_7N_3$: C, 57.3; H, 4.1. Found: C, 57.3; H, 4.3.

Flavothebaone trimethyl ether ψ-methine methohydroxide. (a) The ψ-methine methiodide (83 g.) and silver oxide (from 93 g. silver nitrate and 500 ml. 3*N* sodium hydroxide) were stirred together in water (6 l.) until the water no longer gave a precipitate with silver nitrate. The solution was filtered and the residue well washed with water. The combined filtrate and washings on evaporation afforded 69 g. (98%) of the methohydroxide as a reddish, viscous oil. A portion of this gave a quantitative yield of the ψ-methine methoperchlorate (see above) on treatment with perchloric acid.

(b) Flavothebaone trimethyl ether methine methiodide (10 g.) in water (1 l.) was heated with 50% aqueous potassium hydroxide (75 ml.) for 6 hr. under reflux. The solution was cooled and shaken with ether, when a crystalline solid separated. This was collected, washed, and dried; yield 7.6 g. This substance was insoluble in benzene, but readily dissolved in warm water to give a strongly alkaline solution, which formed salts on treatment with hydriodic and perchloric acids. The salts obtained in this way were identical with the ψ-methine methiodide and methoperchlorate prepared from the ψ-methine, and the crystalline solid must therefore be the ψ-methine methohydroxide. A solution of the salt in dilute nitric acid gave only a faint precipitate of silver iodide on treatment with silver nitrate. No difference was noted between the results obtained by the dry-distillation of the quaternary hydroxides prepared in the above two ways.

Hofmann degradation of flavothebaone trimethyl ether ψ-methine methohydroxide. The methohydroxide (69 g.) was heated *in vacuo*, when decomposition began at 190° (bath temp.) and the temperature was slowly raised to 210° and maintained there for 30 min. The residue of the decomposition (62 g.) was thoroughly extracted with ether, leaving 18.6 g. of insoluble polymerized material, which was not further studied. The combined ether extracts were washed with *N* hydrochloric acid, and in this way 13 g. of basic material was obtained, and from this 8.4 g. of pure ψ-methine base was isolated. The acid-washed extract was washed with water, dried (Na_2SO_4), and evaporated, leaving 25.2 g. of neutral material.

The neutral product was dissolved in benzene (400 ml.) and light petroleum (b.p. 60–80°) added until a faintly turbid solution was obtained, and this was then chromatographed on alumina (750 g.). Elution of the column afforded the following fractions.

(a) 7.17 g. eluted by 13.5 l. of 50:50 mixture of benzene and light petroleum (b.p. 60–80°).

(b) 5.7 g. eluted by 15.0 l. of 65:35 mixture of benzene and light petroleum.

(c) 1.96 g. eluted by 10.0 l. of 80:20 mixture of benzene and light petroleum.

(d) 6.06 g. eluted by 16.0 l. of benzene.

(e) 2.25 g. eluted by benzene containing up to 10% of chloroform.

Fraction (a) on repeated fractional crystallization from methanol afforded Compound D, m.p. 150–152° and a small amount of Compound C, m.p. 174–175°. Fraction (b) yielded Compound D and larger amounts of Compound C, together with a small amount of Compound B, m.p. 178–179°. Fractions (c) and (d) afforded principally Compound B and, from the mother liquors of the recrystallization of this, a very small quantity of Compound F, m.p. 220–235°. Fraction (e) consisted only of intractable material.

Compound B. This substance, 11-acetyl-1,2,7,10-tetramethoxychrysofluorene, was obtained as yellow prisms, m.p. 178–179°, $[\alpha]^{20}_{D}$ 0.0° (EtOH, $CHCl_3$) on recrystallization from methanol, mol. wt. 380 ± 7. It was shown by mixed melting point of the parent compound and of its complexes with 1,3,5-trinitrobenzene and picric acid, to be identical with Compound B prepared by the acetolysis of flavothebaone trimethyl ether ψ-methine methiodide.

Compound C. This substance, which has been shown to be *1,2,7,10-tetramethoxy-11-methylchrysofluorene,* was obtained as yellow rhombohedral plates, m.p. 174–175°, $[\alpha]^{20}_{D}$ 0.0° (EtOH, $CHCl_3$), on recrystallization from methanol or light petroleum (b.p. 100–120°).

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.4; H, 6.3; mol. wt. 350. Found: C, 75.1; H, 6.2; mol. wt. (crystallographic) 348 ± 4.

The *1,3,5-trinitrobenzene complex*, prepared in ethanol and recrystallized from the same solvent, was obtained as deep red-brown prisms, m.p. 171°.

Anal. Calcd. for $C_{22}H_{22}O_4.C_6H_3O_6N_3$: C, 59.7; H, 4.4; N, 7.5. Found: C, 59.9; H, 4.5; N, 7.5.

The *2,4,6-trinitrotoluene complex*, prepared in and recrystallized from ethanol, was obtained as dark red prisms, m.p. 130–131°.

Anal. Calcd. for $C_{22}H_{22}O_4 \cdot C_7H_5O_6N_3$: C, 60.2; H, 4.7; N, 7.3. Found: C, 60 1; H, 4.5; N, 7.0.

The *picrate*, prepared in ethanol, was obtained as dark brown prisms, m.p. 147–148°. It could not be recrystallized from ethanol except in the presence of picric acid.

Anal. Calcd. for $C_{22}H_{22}O_4 \cdot C_6H_3O_6N_3$: C, 58.0; H, 4.3; N, 7.3. Found: C, 58.0; H, 4.3; N, 7.3.

Compound D, which has been shown to be *1,2,7,10-tetramethoxychrysofluorene*, was obtained as almost colorless prisms, m.p. 159° with a transition to colorless needles at 135°, from ethanol (the needle form is obtained initially on cooling the hot alcoholic solution) and as yellow prisms, m.p. 152° from light petroleum (b.p. 100–120°). The identity of the two forms was demonstrated by the infrared spectra in chloroform and in carbon disulfide solution.

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 75.0; H, 5.9; mol. wt., 336. Found: C, 74.8; H, 6.0; mol. wt. (crystallographic) 333 ± 6.

The *1,3,5-trinitrobenzene complex*, prepared in ethanol and recrystallized from isobutanol, was obtained as red needles, m.p. 182°.

Anal. Calcd. for $C_{21}H_{20}O_4 \cdot C_6H_3O_6N_3$: C, 59.0; H, 4.3; N, 7.6. Found: C, 59.3; H, 4.5; N, 7.3.

The *2,4,6-trinitrotoluene complex*, prepared in and recrystallized from ethanol, was obtained as deep red needles, m.p. 139°.

Anal. Calcd. for $C_{21}H_{20}O_4 \cdot C_7H_5O_6N_3$: C, 59.6; H, 4.4; N, 7.5. Found: C, 59.6; H, 4.5; N, 7.3.

The *picrate*, prepared in ethanol, was obtained as dark brown needles, m.p. 173°. This complex could only be recrystallized from ethanol in the presence of picric acid.

Anal. Calcd. for $C_{21}H_{20}O_4{\cdot}C_6H_3O_7N_3$: C, 57.3; H, 4.1; N, 7.4. Found: C, 57.1; H, 4.1; N, 7.2.

Compound F, presumed to be *1,β-anhydro-11-acetyl-12-β-hydroxyethyl-1-hydroxy-2,7,10-trimethoxy-12,13-dihydrochrysofluorene*, was obtained as colorless plates, m.p. 247–248°, $[\alpha]^{20}_D$ +764° ($CHCl_3$, c 1.98), on sublimation and recrystallization from methanol.

Anal. Calcd. for $C_{24}H_{24}O_5$: C, 73.5; H, 6.1; (3) OMe, 23.8, (1) C—CH_3, 3.8. Found: C, 73.6; H, 5.8; OMe, 26.0; C—CH_3, 3.8.

Conversion of compound B into compound D. A mixture of Compound B (0.15 g.), sodium ethoxide (from 0.05 g. sodium and 3 ml. ethanol), and ethanol (12 ml.) was heated under reflux on the water bath for 2 hr. On cooling the mixture yellow prisms, m.p. 154–158°, separated. These were collected and recrystallized from ethanol, when Compound D (identified by infrared spectrum), m.p. 158–159°, was obtained. Another substance, having the properties of sodium acetate, was obtained from the mother liquors.

Conversion of compound D into compound C. Compound D (200 mg.) was added to a solution of sodium (20 mg.) in anhydrous methanol (12 ml.) and the mixture heated in a sealed tube for 16 hr. at 210°. The contents of the tube were poured into water, the mixture acidified with dilute hydrochloric acid, and extracted with benzene. The benzene extract was washed with water and dried over sodium sulfate, concentrated to 15 ml., light petroleum was added until a faintly turbid solution was obtained, and this was chromatographed on alumina. A blue fluorescent band was eluted with a 1:1 mixture of benzene and light petroleum (b.p. 50–60°) and with benzene. Evaporation of the eluates afforded a yellow oil, which crystallized from methanol to give 30 mg. of Compound C as yellow prisms, m.p. 174–175°, undepressed on mixing with Compound C obtained by the Hofmann degradation of the ψ-methine methohydroxide. The 1,3,5-trinitrobenzene complex was obtained as deep red prisms, m.p. 171° alone or mixed with the authentic complex of Compound C.

Attempted conversion of compound D into compound B. Dry methanol (1.5 ml.) was added slowly to powdered potassium (0.07 g.) in dry ether (10 ml.), and the mixture finally evaporated to dryness *in vacuo*, the temperature being raised to 150.° After cooling dry ether (25 ml.) was added to the potassium ethoxide, followed by Compound D (0.5 g.) and dry ethyl acetate (0.4 g.) and the mixture, which rapidly turned dark brown-green, was refluxed for 6 hr. The ether was evaporated and water added to the residue, the dark brown amorphous material was collected, washed with water, dried, dissolved in benzene, and chromatographed on alumina. Fractions were eluted with benzene and with benzene containing 2% of chloroform. The former solvent eluted a blue fluorescent band and from the eluate 0.12 g. of Compound D was obtained. A deep red band was eluted by benzene-chloroform and the eluate afforded 0.15 g. of *1,2,7,10-tetramethoxy-11-oxochrysofluorene*, obtained as orange needles, m.p. 186° on recrystallization first from ethanol and finally from light petroleum (b.p. 100–120°).

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 72.0; H, 5.1. Found: C, 71.9, 72.2; H, 5.0, 5.1.

This substance gives an intense blue solution in concentrated sulfuric acid. No other crystalline material could be recovered from the alumina.

Flavothebaone trimethyl ether methine methohydroxide. Flavothebaone trimethyl ether methine methiodide (25 g.) and silver oxide (from 28.1 g. silver nitrate) were stirred together in water (2 l.) until the aqueous solution no longer gave a precipitate with silver nitrate. The solution was filtered and the filtrate and washings evaporated to dryness *in vacuo* below 50°, when the methohydroxide was obtained, yield 20.1 g. The *methoperchlorate* was obtained on addition of perchloric acid to a solution of the methohydroxide (1 g.) in water (20 ml.). On recrystallization from 50% ethanol it was obtained as light yellow prisms, m.p. 234–235°. The ultraviolet spectrum (λ_{max} 2700 and 3100 Å; ϵ_{max} 4476 and 1841) and the infrared spectrum (carbonyl band 5.96 μ, 1678 cm.$^{-1}$) showed that this is a true derivative of the methine, and that conversion to the ψ-methine has not taken place).

Anal. Calcd. for $C_{28}H_{31}O_5N{\cdot}CH_3ClO_4$: C, 60.4; H, 5.9; Cl, 6.2. Found: C, 60.1; H, 5.6; Cl, 6.5.

Hofmann degradation of flavothebaone trimethyl ether methine methohydroxide. The methohydroxide (19.0 g.) was decomposed at 180–190° and the temperature slowly raised to 220° over 1 hr. The residue of the decomposition (17 g.) was separated into the following fractions:

(a) Polymerized material (3.5 g.).

(b) Basic material (4.15 g.) from which only flavothebaone trimethyl ether ψ-methine, m.p. 187°, could be obtained.

(c) Neutral material (8.6 g.).

The neutral material in benzene (150 ml.) and light petroleum (b.p. 60–80°) (100 ml.) was chromatographed on alumina (250 g.). A total of 6.72 g. of material was eluted from the column with solvents varying in composition from 1:1 benzene-light petroleum (b.p. 60–80°) to benzene containing 5% of chloroform as in the chromatographic separation of the products of the degradation of the ψ-methine methohydroxide. Compounds B, C, and D were recovered from the eluates. No other crystalline product could be isolated.

Hofmann degradation of flavothebaone trimethyl ether methine methiodide by Mosettig's[17] *method.* Flavothebaone trimethyl ether methine methiodide (40 g.) was added in portions over 30 min. to a boiling stirred solution of sodium (10 g.) in cyclohexanol (500 ml.) under an atmosphere of nitrogen. The solution became dark orange, but the color faded to straw yellow progressively as the solution was boiled for 3 hr. The cyclohexanol was removed by steam distillation leaving a suspension of oily droplets, that solidified on cooling. The solid was collected and dissolved in ether to give a dark brown solution that became yellow on shaking with aqueous sodium dithionite. The ether solution was washed twice with dilute hydrochloric acid, once with water, and dried. The acid washings on neutralization with ammonia afforded an intractable yellow base that very readily darkened on exposure to the air. This may consist of partially demethylated ψ-methine.

The ether extract on evaporation afforded a brownish-yellow gum (20 g.) that partially crystallized on trituration with ethanol (100 ml.). The solid was collected and recrystallized from ethanol, when it was obtained as brown needles, m.p. 150–151°. It was purified by dissolving in benzene and passing through a short column of alumina, after which Compound—D was obtained as colorless prisms, m.p. 159°, undepressed on mixing with an authentic specimen.

The mother liquors from the isolation of Compound D were evaporated and the residue dissolved in a 1:1 mixture of benzene and light petroleum (b.p. 60–80°) and chromatographed on alumina. From the eluates the only crystalline substance that could be isolated was Compound D. A considerable amount of the high-boiling by-product previously obtained in this type of degradation,[18,19] was recovered.

Repetition of the above degradation using flavothebaone trimethyl ether methine methiodide (40 g.) and a hot solution of potassium hydroxide (23 g.) in cyclohexanol (500 ml.) and water (20 ml.) afforded 25 g. of crude neutral material, which on recrystallization from ethanol yielded Compound E (3.3 g.) as white needles, m.p. 194°, $[\alpha]^{20}_D$ −292.5°

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(17) Mosettig and Meitzner, *J. Am. Chem. Soc.*, **56**, 2738 (1934).

(18) L. F. Small, *J. Org. Chem.*, **7**, 158 (1942).

(19) K. W. Bentley and A. F. Thomas, *J. Chem. Soc.*, 3237 (1955).

($CHCl_3$, c 1.70). λ_{max} 2250, 2650, and 3050 Å; ϵ_{max} 31,750, 17,830, and 7244.

Anal. Calcd. for $C_{25}H_{26}O_5$: C, 73.9; H, 6.4; Found: C, 74.0, 73.6; H, 6.4, 6.3.

Evaporation of the mother liquors from the recrystallizations of Compound E followed by chromatographic separation of the residue afforded ultimately 1 g. of Compound D and a further 0.5 g. of Compound E. Further quantities of Compound D must have been contained in the several intractable fractions as these gave the trinitrobenzene complex of this compound (m.p. 180°) on treatment with 1,3,5-trinitrobenzene.

Hofmann degradation of flavothebaone trimethyl ether ψ-methine methiodide by Mosettig's method. Flavothebaone trimethyl ether ψ-methine methiodide (10 g.) was degraded as above by heating with a solution of sodium (3 g.) in cyclohexanol (125 ml.) and water (15 ml.). From the products of degradation 0.52 g. of pure Compound E was recovered.

Hydrogenation of Compound E. Compound E (0.4 g.) in glacial acetic acid (10 ml.) was shaken with hydrogen at room temperature and pressure in the presence of platinum oxide (0.06 g.) when one mole of hydrogen was absorbed in 10 min., after which absorption ceased. The catalyst was removed, the filtrate concentrated *in vacuo* and water added. The product was collected and washed with water, yield quantitative. Recrystallization of the product from ethanol afforded *dihydro-Compound E* as colorless needles, m.p. 152–153°, $[\alpha]^{19}_{D}$ −67.8° ($CHCl_3$, c 1.15). λ_{max} 2250, 2750, and 3050 Å, ϵ_{max} 22,390, 12,880, and 4677.

Anal. Calcd. for $C_{25}H_{28}O_5$: C, 73.5; H, 6.9. Found: C, 73.6, 73.3, 73.5; H, 6.9, 6.9, 6.8.

Reduction of flavothebaone trimethyl ether ψ-methine with sodium and liquid ammonia. A solution of flavothebaone trimethyl ether ψ-methine (5 g.) in 2-ethoxyethanol (100 ml.) was added with stirring to liquid ammonia (500 ml.) in a 1 liter Dewar flask. Thin slices of sodium (12 g.) were added over a period of 30 min. after which a permanent blue color developed. This color was discharged by the addition of a small quantity of ethanol and the solution was then poured into water. The reduction product was extracted with ether to give the crude base as a yellow oil; this was dissolved in ethanol and converted into the perchlorate. The base was recovered from a hot solution of the recrystallized perchlorate by the addition of dilute aqueous sodium carbonate. On recrystallization from 50% ethanol *flavothebaone trimethyl ether desmethoxydesoxodihydro-ψ-methine* was obtained as white prisms, m.p. 139–140°, $[\alpha]^{20}_{D}$ −63.6° ($CHCl_3$, c 0.57).

Anal. Calcd. for $C_{26}H_{35}O_3N$: C, 76.2; H, 8.6; N, 3.4. Found: C, 76.2; H, 8.8; N, 3.6.

The *perchlorate*, prepared in and recrystallized from ethanol, was obtained as white prisms, m.p. 269° (dec.), $[\alpha]^{22}_{D}$ −66.8° ($CHCl_3$, c. 0.54).

Anal. Calcd. for $C_{26}H_{35}O_3N \cdot HClO_4$: C, 61.2; H, 7.1; Cl 7.0; Found: C, 61.3; H, 6.9; Cl, 7.3.

The *picrate*, prepared in and recrystallized from ethanol, was obtained as yellow prisms, m.p. 237°.

Anal. Calcd. for $C_{26}H_{35}O_3N \cdot C_6H_3O_7N_3$: C, 60.2; H, 6.2. Found: C, 60.2; H, 6.0.

Degradation of flavothebaone trimethyl ether desmethoxydesoxodihydro-ψ-methine N-oxide. Flavothebaone trimethyl ether desmethoxydesoxydihydro-ψ-methine (5 g.) and 30% hydrogen peroxide (10 ml.) were heated together on the steam bath for 30 min.; acetone was then added to form a homogeneous solution, which was heated for a further 10 min. and then evaporated to dryness at 100°/20 mm. The N-oxide was then decomposed by heating at 140–150°/1.5 mm. for 15 min., a dark brown residue being obtained. This was extracted with benzene, and the benzene solution washed with dilute hydrochloric acid and water, and dried over sodium sulfate. The solution was then concentrated to 10 ml., light petroleum (b.p. 60–60°) was added until a faint turbidity was produced and the mixture was then chromatographed on alumina. Elution of a blue fluorescent band with a 1:1 mixture of benzene and light petroleum (b.p. 50–60°) afforded *flavothebaone trimethyl ether desmethoxydesoxodihydrodesaza-ψ-methine* which, on recrystallization from methanol, was obtained as white needles, m.p. 144°, $[\alpha]^{20}_{D}$ −85.6° ($CHCl_3$, c 1.48). λ_{max} 2800 Å, ϵ_{max} 6,400.

Anal. Calcd. for $C_{24}H_{28}O_3$: C, 79.1; H, 7.7; (3) OMe, 25.6. Found: C, 79.4; H, 7.7; OMe, 26.1.

Reduction of flavothebaone trimethyl ether desmethoxydesoxodihydrodesaza-ψ-methine. The desmethoxydesoxodihydrodesaza-ψ-methine (0.36 g.) in acetic acid (10 ml.) was hydrogenated over platinum oxide (0.05 g.) when 1 mol. equiv. of hydrogen was absorbed. The catalyst was removed by filtration, and the product precipitated from the filtrate by the addition of water, collected, and recrystallized from ethanol, when *flavothebaone trimethyl ether desmethoxydesoxotetrahydrodesaza-ψ-methine* was obtained as white needles, m.p. 180–181° $[\alpha]^{20}_{D}$ −76.8° ($CHCl_3$, c 0.90).

Anal. Calcd. for $C_{24}H_{30}O_3$: 78.7; H, 8.3; (3) OMe, 25.4. Found: C, 78.8; H, 8.3; OMe, 25.7.

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