[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF ABERDEEN,
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Flavothebaone. Part I. Preliminary Work: Spectral Studies and Acetolysis

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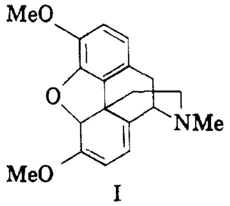
The acetolysis of flavothebaone trimethyl ether methine and of flavothebaone trimethyl ether has been studied. The methine base has been shown to undergo recyclization of the nitrogen-containing ring under these conditions, only a very small amount of nitrogen-free product being obtained. On the basis of these results and of spectral studies a part-structure for flavothebaone is advanced.

Thebaine (I) readily condenses with *p*-benzoquinone to give an adduct that is easily enolized to the quinol (II), which is transformed into flavothebaone on heating with concentrated hydrochloric acid. This base has been studied by Schöpf, von Gottberg, and Petri[1] who allotted to it the composition $C_{24}H_{23}NO_5$, and showed that it contains three phenolic hydroxyl groups and one reducible double bond, present in an α,β-unsaturated ketone system. One of the most striking features of the base is that it gives an intensely orange-red solution in alkalis, whereas dihydroflavothebaone remains colorless under these conditions. This led Schöpf and his co-workers to the conclusion that the α,β-unsaturated ketone system is directly conjugated with the quinol nucleus in flavothebaone, for which they were unable to suggest an acceptable structure, though they suggested that it might contain the part-structure (III). A study of the oxidation and Beckmann transformation of certain flavothebaone derivatives failed to clarify the position.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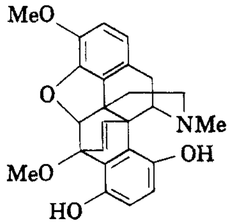
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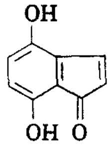
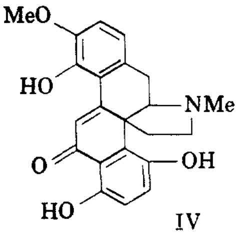

III

We initially believed that the structure (IV), for the production of which from the quinol (II) a feasible mechanism could be advanced,[2] would give an acceptable explanation of the color of flavothebaone in alkalis. The structure (IV) corresponds to the composition $C_{22}H_{21}NO_5$ with which most of Schöpf's analytical data could be reconciled by varying the degree of solvation. Crystallographic determination of the molecular weights of solvated flavothebaone trimethyl ether (448 ± 12; $C_{27}H_{29}NO_5\cdot{}^1/_2MeOH = 462.5$; $C_{25}H_{27}NO_5\cdot{}^1/_2MeOH = 436.5$) and flavothebaone trimethyl ether methine (449 ± 14; $C_{28}H_{31}NO_5 = 461$; $C_{26}H_{29}NO_5 = 435$) failed to allow a distinction between the two possibilities, and attention was accordingly directed to a study of the degradation of flavothebaone trimethyl ether.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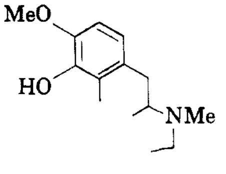
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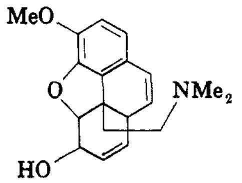
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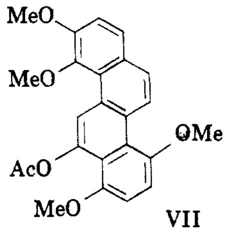
VII

The ultraviolet spectrum of flavothebaone trimethyl ether methine is a close summation of those of flavothebaone trimethyl ether and α-codeimethine (VI) (Fig. 1), from which we may conclude that flavothebaone contains the system (V). The trimethyl ether methiodide of (IV), or of the derived methine, would be expected to suffer degradation to the chrysene derivative (VII) on heating with acetic anhydride [*Cf.* the facile degradation of the base (VIII) to the phenanthrene (IX)[3]], but flavothebaone trimethyl ether methiodide, the derived methine base, and its methiodide under these conditions afford principally a mixture of flavothebaone trimethyl ether and the methine base, together with a very small amount of a nitrogen-free substance—Compound-A.

The recyclization of the methine base during acetolysis is without precedent in the morphine-

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[1] Schöpf, von Gottberg, and Petri, *Ann.*, **536**, 216 (1938).

[2] Bentley, *The Chemistry of The Morphine Alkaloids*, The Clarendon Press, Oxford, 1954, p. 295.

[3] Goto, Arai, and Odera, *Bull. Chem. Soc. Japan*, **17**, 393 (1942).

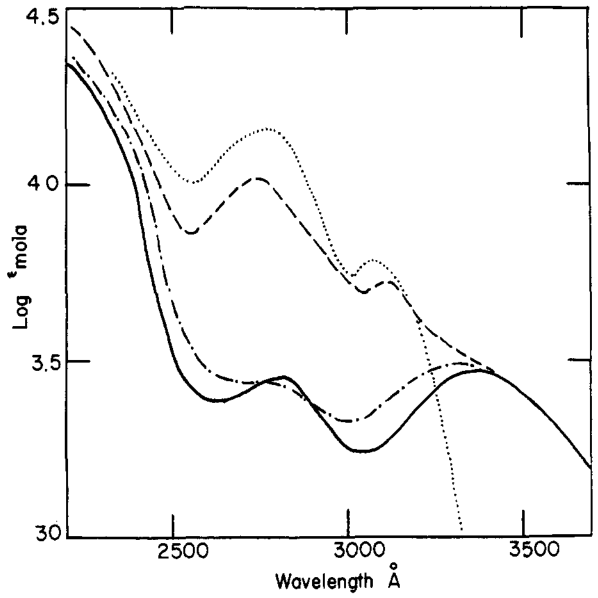
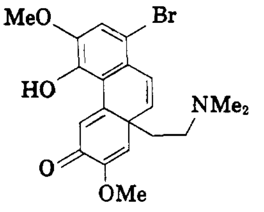
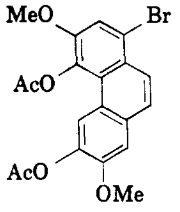


FIG. 1.—ULTRAVIOLET SPECTRA. ——— Flavothebaone trimethyl ether; – – – – Flavothebaone trimethyl ether methine; .... α-Codeimethine; –.–.–.–. Compound-A.



VIII



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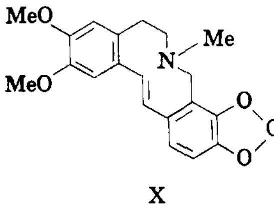
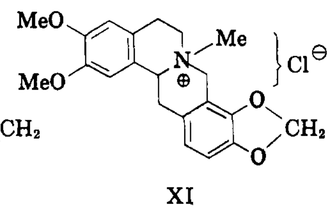
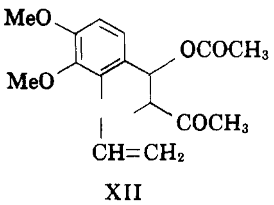


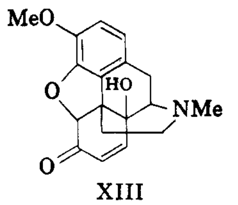
X



XI



XII



XIII

thebaine group of alkaloids, and there is no precise analogy in the literature, though it may be compared with the conversion of anhydrodihydrocryptopine-A (X) into *iso*dihydrocryptopine chloride (XI) on heating with hydrochloric acid.

The nitrogen-free substance—Compound-A—has the composition $C_{30}H_{30}O_8$, and its ultraviolet spectrum (Fig. 1) is very similar to that of flavothebaone trimethyl ether (*i.e.* the styrenoid chromophore present in the methine base has disappeared). It contains one unsaturated and one saturated carbonyl group (infrared bands at 5.75 μ and 5.96 μ) an aliphatic acetoxy group (band at 8.07 μ) and a vinyl group (band at 10.85 μ), and clearly must arise from the methine base by the addition of Ac_2O to the styrenoid double bond and the degradation of $—CH_2CH_2NMe_2$ to $—CH{=}CH_2$, and the part-structure (XII) may be allotted to it.

The results of the acetolysis show that the ring system of flavothebaone is extremely stable towards acid degradation, and strongly suggest that an aromatization-blocking group is present at an angular position in the molecule, presumably the quinol nucleus at $C_{(14)}$ [compare the stability of 14-hydroxycodeinone (XIII) and its derivatives], and such a blocking group is not present in IV.

Assuming that the basic phenanthrene skeleton of thebaine (I) survives intact in flavothebaone (we have been unable to detect any C_2 fragment corresponding to that which would be lost in going from II to IV), if the quinol group remains attached to $C_{(14)}$ as indicated above, the part structure (III) suggested by Schöpf[1] cannot be present in flavothebaone; we have confirmed this by an examination of dihydroflavothebaone trimethyl ether, the infrared spectrum of which shows a carbonyl absorption band at 5.85 μ, indicating that the compound is not an aromatic ketone. This band also shows that the carbonyl group is present in a six-membered ring. That neither flavothebaone nor dihydroflavothebaone contain the system $Ar—CH_2—CO—$ is demonstrated by the absence of absorption bands at 13.3 μ and 14.4 μ, characteristic of this system, in the infrared spectra of these bases.

The keto-group of flavothebaone could be present at $C_{(6)}$, at $C_{(8)}$ (by an allylic migration), or at $C_{(5)}$. Location of the group at $C_{(5)}$ would provide something to relate to the opening of the oxide ring, but leads to unacceptable structures for the base, as

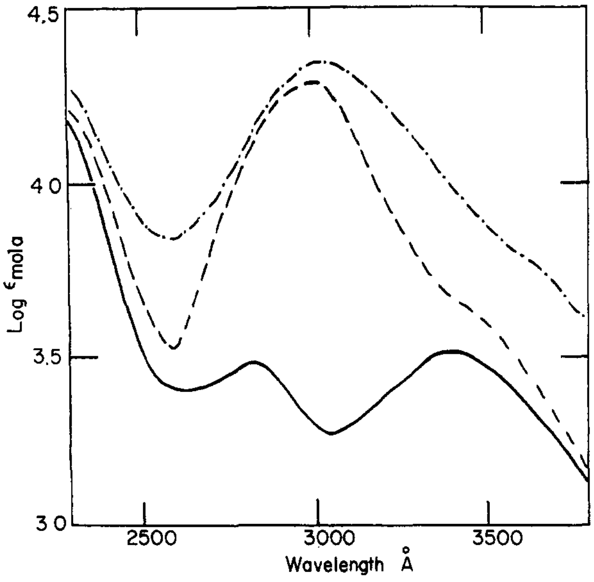
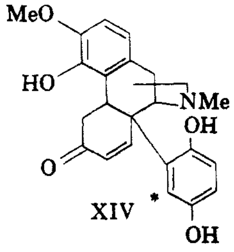
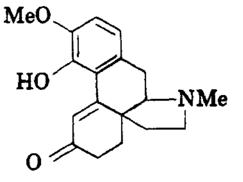


FIG. 2.—ULTRAVIOLET SPECTRA. ——— Flavothebaone trimethyl ether; – – – – Metathebainone; –·–·–· 2′,3′-Dimethoxybenzylidene-2,5-dimethoxyacetophenone.

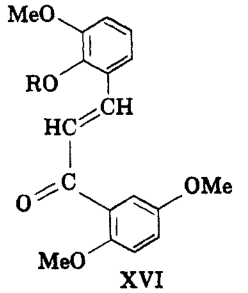
does location of the carbonyl group at $C_{(8)}$; accordingly this group is assumed to be at $C_{(6)}$. As flavothebaone is an α,β-unsaturated ketone the double bond can be placed at $C_{(7)} : C_{(8)}$ and the part-structure (XIV) may be adopted for this. The placing of the double bond at $C_{(5)} : C_{(13)}$ need not be contemplated as the ultraviolet spectrum of flavothebaone bears no resemblance to that of metathebainone (XV) (Fig. 2) and as the double bond of flavothebaone is much more easily reduced than that of metathebainone. It may be noted that the extension of the chromophoric system of metathebainone to that of the structure (IV) has little effect on the ultraviolet spectrum, as the spectra of 2′-hydroxy-3′-methoxybenzylidene-2,5-dimethoxyacetophenone (XVI, R = H) and its methyl ether (XVI, R = Me) closely resemble that of metathebainone (Fig. 2).



XIV



XV



XVI

It would be impossible to introduce another double bond into XIV out of conjugation with the guaiacol nucleus and, as the ultraviolet spectrum of dihydroflavothebaone trimethyl ether is virtually the same as that of dihydro-thebainequinol (the dihydro-derivative of II) (Fig. 3), no such bond can be present in flavothebaone, which must accordingly contain another ring in XIV connecting the quinol nucleus at the point marked by an asterisk with a carbon atom of the phenanthrene nucleus. Positions 7 and 10 are excluded for this, as they would involve a double bond at a bridge-head in flavothebaone or in the trimethyl ether methine, and position 9 may be excluded as flavothebaone trimethyl ether reacts with cyanogen bromide without scission of the nitrogen-containing ring, NMe being simply replaced by NCN. Of the available positions 5, 8, and 13 linkage to $C_{(8)}$ would satisfy the apparent requirement of conjugation of the α,β-unsaturated ketone system with the quinol nucleus (orange-red sodium salt), but on steric and mechanistic grounds the most acceptable position for the linkage is $C_{(5)}$, in which case the nitrogen-containing side-chain can remain at $C_{(13)}$. This view will be developed in a subsequent communication.[4]

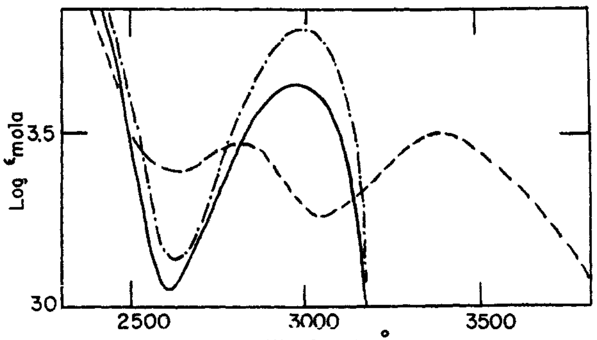


FIG. 3.—ULTRAVIOLET SPECTRA. ———— Dihydroflavothebaone trimethyl ether; – – – – Flavothebaone trimethyl ether; –·–·–·– Dihydro-thebainequinol

Thebaine has been condensed with *p*-toluquinone, and the adduct enolized to the quinol analog of II, which has been transformed into methylflavothebaone and methylflavothebaone trimethyl ether methine.

EXPERIMENTAL

Flavothebaone. (*a*). Thebainequinol (25 g.) and glacial acetic acid (100 ml.) were heated on the water-bath for one hour with a slow addition of concentrated hydrochloric acid (500 ml.). The mixture then was heated for a further three hours and the crystalline acid hydrochloride was collected.

(*b*). Thebainequinol (2 g.) was heated with 40% sulfuric acid (20 ml.) on the water-bath for four hours, and the crystalline material that separated was collected and recrystallized from water, when *flavothebaone hydrosulfate* was obtained as yellow prisms, (m.p. 337–339° dec.).

Anal. Calc'd for $C_{24}H_{23}NO_5 \cdot H_2SO_4 \cdot H_2O$: C, 55.3; H, 5.2; Loss, 3.5. Found: C, 55.2; H, 5.2; Loss, 3.0.

(*c*). Thebaine-quinone (50 g.) in glacial acetic acid (200 ml.) was heated on the water-bath for four hours with concentrated hydrochloric acid (750 ml.), and the acid hydrochloride of flavothebaone was collected, yield 61 g.

(*d*). Thebaine-quinone (10 g.) and 40% sulphuric acid (200 ml.) were heated together on the water-bath for five hours, the mixture was cooled, and the flavothebaone hydrosulfate was collected.

The base recovered from the salts prepared as in (*a*)–(*d*) above by neutralization with ammonia was obtained as yellow prisms m.p. 255° (lit. m.p. 255–257°), and on recrystallization from methanol it was recovered as yellow prisms m.p. 203° (lit. m.p. 200–206°).

The *perchlorate* was prepared in and recrystallized from ethanol, when it was obtained as pale yellow elongated prisms, m.p. 270–272°.

Anal. Calc'd for $C_{24}H_{23}NO_5 \cdot HClO_4$: C, 56.9; H, 5.0; Cl, 7.0. Found: C, 56.3; H, 5.3; Cl, 7.1.

The *picrate*, prepared from the hydrochloride and sodium picrate, was obtained as bright yellow needles, m.p. 240–242° on recrystallization from ethanol.

Anal. Calc'd for $C_{24}H_{23}NO_5 \cdot C_6H_3N_3O_7 \cdot H_2O$: C, 55.25; H, 4.3; N, 8.6; Loss, 2.8. Found: C, 55.25; H, 4.2; N, 8.5; Loss, 2.4.

The *hydrazone dihydrochloride* was obtained as ruby red prisms, m.p. 323° (dec.) on heating a solution of flavothe-

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(4) *Cf.* Bentley, Ref. (2) p. 297, lines 21–24.

baone hydrochloride and hydrazine hydrochloride in dilute hydrochloric acid.

Anal. Calc'd for $C_{24}H_{25}N_3O_4 \cdot 2HCl \cdot H_2O$: C, 57.6; H, 5.8. Found: C, 57.3; H, 6.0.

Triacetylflavothebaone. (*a*). Flavothebaone (4 g.), acetic anhydride (120 ml.), and sodium acetate (0.8 g.) were heated together under reflux for six hours. The product, which was obtained as a white solid, m.p. 250–253°, could not be recrystallized from benzene, but was obtained as colorless needles, m.p. 253° on recrystallization from ethanol.

Anal. Calc'd for $C_{30}H_{29}NO_8$: C, 67.7; H, 5.5. Found: C, 67.4; H, 5.5.

(*b*). Flavothebaone (1.5 g.), acetic anhydride (7 ml.), and pyridine (50 ml.) were allowed to stand at room temperature for three hours. On isolation and recrystallization from ethanol triacetylflavothebaone was obtained as colorless needles, m.p. 253°, alone or mixed with a specimen prepared as in (*a*). Schöpf[1] reported the production by both these methods of a crude product m.p. 270° obtained as colorless needles, m.p. 273° on recrystallization from benzene.

Flavothebaone trimethyl ether. This was prepared from flavothebaone and phenyltrimethylammonium chloride according to the directions of Schöpf.[1] It was obtained as almost colorless plates, m.p. 252° (lit. m.p. 253°) on recrystallization from ethanol $[\alpha]^{20}_{D}$ +178° ($CHCl_3$, *c*, 0.74).

The *perchlorate*, prepared in ethanol and recrystallized from 80% ethanol, was obtained as irregular prisms, m.p. 263–265° (dec.).

Anal. Calc'd for $C_{27}H_{29}NO_5 \cdot HClO_4$: C, 59.1; H, 5.5; Cl, 6.5. Found: C, 59.4; H, 6.0; Cl, 6.4.

Flavothebaone trimethyl ether methine. This base was prepared by the Hofmann degradation of flavothebaone trimethyl ether methiodide according to the directions of Schöpf[1] and was obtained as almost colorless crystals, rapidly turning deep orange on exposure to sunlight, m.p. 159–160° (lit. 160–161°). $[\alpha]^{20}_{D}$ −125.6° ($CHCl_3$, *c*, 1.48). Methiodide, m.p. 290–293° (lit. 295°), $[\alpha]^{20}_{D}$ −104.7° (water, *c*, 0.63).

The *perchlorate*, prepared in ethanol and recrystallized from 75% ethanol was obtained as very pale yellow irregular plates, m.p. 272° (dec.).

Anal. Calc'd for $C_{28}H_{31}NO_5 \cdot HClO_4 \cdot {}^1/_2H_2O$: C, 58.8; H, 5.8; Loss, 1.6. Found: C, 58.6; H, 6.0; Loss, 1.2.

The *picrate*, prepared in ethanol and recrystallized from isoamyl alcohol, was obtained as yellow plates, m.p. 193°.

Anal. Calc'd for $C_{28}H_{21}NO_5 \cdot C_6H_3N_3O_7$: C, 59.2; H, 4.9; N, 8.1. Found: C, 59.1; H, 5.0; N, 7.8.

The *oxime* was prepared by heating a mixture of the base and hydroxylamine hydrochloride in water under reflux for two hours, cooling, neutralizing with ammonia, and recrystallizing the product from 75% ethanol. It was obtained as colorless minute prisms, m.p. 252–253°.

Anal. Calc'd for $C_{28}H_{32}N_2O_5 \cdot {}^1/_2H_2O$: C, 69.3; H, 6.8. Found: C, 69.3; H, 6.9.

Acetolysis of flavothebaone trimethyl ether methiodide. Flavothebaone trimethyl ether methiodide (13.3 g.), fused sodium acetate (4 g.), and acetic anhydride (160 ml.) were boiled under reflux for one hour, silver acetate (3.76 g.) was added, and the mixture was heated under reflux for a further four hours. The silver iodide was removed by filtration and the filtrate was heated in sealed tubes at 180–190° for 48 hours. The tubes when cold were opened carefully without agitation (agitation precipitated violent evolution of a volatile material) and the liquid was filtered from a small amount of charred material and evaporated to dryness leaving a brown resinous residue. This was shaken with water and extracted several times with ether (2 l. total). The ether extract was washed three times with dilute hydrochloric acid, twice with water, and dried. On evaporation of the ether 3.6 g. of *neutral material* was obtained. The aqueous liquor remaining after the ether extraction was filtered and combined with the acid washings and neutralized with ammonia, when a voluminous white precipitate was obtained. This on ether extraction yielded 3.85 g. of a light yellow solid comprising the *basic fraction.*

These two fractions then were investigated as follows.

The neutral material, in solution in a 1:1 mixture of benzene and light petroleum (b.p. 60–80°) was chromatographed on alumina. Elution of the chromatogram was effected as follows:

(*a*). Elution with benzene afforded 0.28 g. of solid, which on recrystallization from methanol yielded 0.18 g. of crystalline material, m.p. 263–267°.

(*b*). Elution with mixtures of benzene and chloroform containing progressively greater proportions of the latter eluted only yellowish intractable oils (2.25 g.) from which finally 0.06 g. of the crystalline solid m.p. 263–267° was eventually recovered by further chromatography.

The crystalline material (total 0.24 g.) was purified by sublimation and by recrystallization from methanol, when *Compound-A* was obtained as colorless needles, m.p. 268°, $[\alpha]^{20}_{D}$ +148.5° ($CHCl_3$, *c*, 1.74).

Anal. Calc'd for $C_{30}H_{30}O_8$: C, 69.5; H, 5.8; (1)OAc, 11.4; (4)OMe, 24.0. Found: C, 70.0; H, 6.0; OAc, 13.0; OMe, 25.0.

The basic fraction. The basic product (3.85 g.) in benzene was chromatographed on alumina, and the chromatogram was eluted with benzene. The first eluates afforded 1.4 g. of colorless crystals, m.p. 240–248°, which on recrystallization from methanol afforded flavothebaone trimethyl ether, identical in every respect with an authentic specimen. Elution of the column with benzene containing 2% of chloroform afforded 0.95 g. of non-crystalline material, which on crystallization from 50% ethanol gave 0.37 g. of flavothebaone trimethyl ether methine, m.p. 159° alone or mixed with an authentic specimen. Elution of the column with solvents containing greater proportions of chloroform resulted in the recovery of 0.33 g. of intractable material.

The acetolysis of flavothebaone trimethyl ether methine. The reaction was carried out as described above, using flavothebaone trimethyl ether methine (3 g.), sodium acetate (1 g.), and acetic anhydride (50 ml.). The following crystalline materials were isolated from the product: flavothebaone trimethyl ether (0.55 g.), flavothebaone trimethyl ether methine (0.51 g.), and Compound-A (0.07 g.).

The acetolysis of flavothebaone trimethyl ether methine methiodide. The reaction was carried out using flavothebaone trimethyl ether methine methiodide (18 g.), sodium acetate (5 g.), acetic anhydride (630 ml.) and silver acetate (4.97 g.). From the product the following crystalline substances were isolated: flavothebaone trimethyl ether (1.1 g.), flavothebaone trimethyl ether methine (1.65 g.), and Compound-A (0.35 g.).

Attempted Huang-Minlon reduction of flavothebaone trimethyl ether. A solution of sodium (0.62 g.) in diethylene glycol (15 ml.) and 85% hydrazine hydrate (10 ml.) were added to a solution of flavothebaone trimethyl ether (4 g.) in diethyl glycol (200 ml.) and the mixture was boiled under reflux for one hour. The condenser was removed and water was allowed to distil from the system until the boiling point rose to 210°, when the mixture was boiled under reflux for four hours. The mixture was evaporated to small bulk *in vacuo*, diluted with water, and extracted with ether. The extract was washed, dried, and evaporated and the residue was dissolved in benzene and chromatographed on alumina.

Elution of the column with benzene afforded a product (0.3 g.) that crystallized from methanol as long colorless needles, m.p. 115°. The analytical data for this (Found: C, 18.2; H, 11.1) indicated that it was derived from the diethylene glycol, and it was accordingly not studied further. Elution of the column with benzene containing 5% of chloroform afforded 3.1 g. of material from which a poor yield of *flavothebaone trimethyl ether hydrazone* was recovered as colorless prisms, m.p. 233–234°, $[\alpha]^{20}_{D}$ +390° ($CHCl_3$, *c*, 2.13) on recrystallization from methanol.

Anal. Calc'd for $C_{27}H_{31}N_3O_4$: C, 70.2; H, 6.8; N, 9.1. Found: C, 70.1; H, 6.6; N, 8.9.

Cyanonorflavothebaone trimethyl ether. Flavothebaone trimethyl ether (2 g.) and cyanogen bromide (2 g.) were allowed to stand overnight in chloroform (40 ml.). The solution was evaporated to dryness *in vacuo* and the residue was recrystallized twice from 2-ethoxyethanol, when it was obtained as colorless needles, m.p. 340–341°.

Anal. Calc'd for $C_{27}H_{26}N_2O_5$: C, 70.7; H, 5.7. Found: C, 70.4; H, 5.8.

$C{\equiv}N$ absorption band in infrared spectrum, 4.56 μ.

2'-Hydroxy-3'-methoxybenzylidene-2,5-dimethoxyacetophenone. To 50% aqueous potassium hydroxide (6 ml.) was added a solution of 2-hydroxy-3-methoxybenzaldehyde (2.53 g.) and 2,5-dimethoxyacetophenone (3.0 g.) in ethanol (50 ml.). The solution was allowed to stand for 48 hours at 35°, after which the precipitated potassium salt was collected, dissolved in water, and decomposed with carbon dioxide. The solid matter was collected and recrystallized from 50% ethanol, when it was obtained as yellow needles, m.p. 123°.

Anal. Calc'd for $C_{18}H_{18}O_5$: C, 68.8; H, 5.8. Found: C, 68.9; H, 5.9.

2',3'-Dimethoxybenzylidene-2,5-dimethoxyacetophenone. Sodium (0.1 g.) in methanol (6 ml.) was added to a hot solution of 2,3-dimethoxybenzaldehyde (0.5 g.) and 2,5-dimethoxyacetophenone (0.54 g.) in ethanol (10 ml.) and after one hour the mixture was poured into water (50 ml.). The precipitate was collected and recrystallized from 50% ethanol, when it was obtained as yellow needles, m.p. 65–66°.

Anal. Calc'd for $C_{19}H_{20}O_5$: C, 69.5; H, 6.1. Found: C, 69.4; H, 6.2.

Thebaine-p-toluquinone. Thebaine (10 g.) and *p*-toluquinone (3.6 g.) in toluene (25 ml.) were heated for 10 min. on the water-bath, and the mixture was cooled and the product was collected. After washing with toluene and ether, it was obtained as pale, fawn-colored prisms, m.p. 203°.

Anal. Calc'd for $C_{26}H_{27}NO_5$: C, 72.0; H, 6.2. Found: C, 71.6; H, 6.0.

Thebainetoluquinol. Thebaine-*p*-toluquinone (10 g.) was heated in boiling 2-ethoxyethanol (40 ml.) and glacial acetic acid (1 ml.) until all the material had dissolved. On cooling the quinol separated, and was obtained as colorless prisms, m.p. 257° on recrystallization from 2-ethoxyethanol.

Anal. Calc'd for $C_{26}H_{27}NO_5$: C, 72.0; H, 6.2. Found: C, 72.0; H, 6.0.

Methylflavothebaone. This base was prepared from thebainetoluquinol (6 g.), glacial acetic acid (10 ml.), and concentrated hydrochloric acid (75 ml.), in a manner analogous to the preparation of flavothebaone.

The *hydrochloride* separated, and was recrystallized from water, when it was obtained as stout bright yellow rhombohedra, m.p. 320°.

Anal. Calc'd for $C_{25}H_{25}NO_5{\cdot}HCl{\cdot}3H_2O$: C, 59.0; H, 6.2; Cl, 6.6; Loss, 10.6. Found: C, 59.0; H, 6.3; Cl, 7.0; Loss, 10.0.

The *base*, obtained from the hydrochloride and ammonia, was recovered as fawn-colored prisms, m.p. 254° on recrystallization from 80% methanol.

Anal. Calc'd for $C_{25}H_{25}NO_5{\cdot}1^1/_2H_2O$: C, 67.1; H, 6.3; Loss, 6.0. Found: C, 66.8; H, 6.1; Loss, 5.9.

The *perchlorate*, prepared in ethanol and recrystallized from water, was obtained as yellow prisms, m.p. 247°.

Anal. Calc'd for $C_{25}H_{25}NO_5{\cdot}HClO_4{\cdot}2H_2O$: C, 53.9; H, 5.2; Loss, 6.5. Found: C, 54.2; H, 5.0; Loss, 6.2.

Methylflavothebaone trimethyl ether methine. Cold 30% aqueous sodium hydroxide was slowly added, with constant shaking, to a mixture of methylflavothebaone hydrochloride (1.5 g.) and methyl sulfate (4.5 ml.), the temperature being kept below 50°. When a homogeneous solution was obtained 10 ml. of 30% sodium hydroxide was added and the mixture was heated on the water-bath for 30 min. An oil separated, and on cooling this solidified. The solid was dissolved in ethanol, 30% perchloric acid was added, and the crystalline solid was collected. On recrystallization from 50% ethanol the *perchlorate* was obtained as almost colorless prisms, m.p. 249–250°.

Anal. Calc'd for $C_{29}H_{33}NO_5{\cdot}HClO_4{\cdot}2^1/_2H_2O$: C, 59.1; H, 6.6; Cl, 6.0. Found: C, 59.2; H, 6.4; Cl, 6.0.

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