Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.66; H, 8.45.

B. From 17α-Ethinyl-17-hydroxyandrost-4-en-3-one *via* Mannich Reaction.—A solution of 14.0 g. of 17α-ethinyl-17-hydroxyandrost-4-en-3-one, 7.0 ml. of 40% aqueous formaldehyde, and 7.0 g. of dimethylamine hydrochloride in 300 ml. of acetic acid was heated in a nitrogen atmosphere at 80° for 1 hr. The reaction mixture was poured into 2 l. of ice-cold water. The resultant precipitate was collected on a filter and dried. This material (1.04 g.) proved to be recovered starting material. The filtrate was made neutral with saturated sodium bicarbonate solution and extracted with methylene dichloride. The organic extract was washed with saturated salt solution, dried (Na_2SO_4), filtered, and evaporated to dryness under reduced pressure to afford 14 g. of a solid. (Purification of a small sample of this base by recrystallization from methylene dichloride was unsuccessful, probably owing to its ready decomposition to the 2-methylene derivative.) The crude Mannich base was decomposed to the 2-methylene derivative by subjecting it to chromatography on 400 g. of Florisil. Elution with methylene dichloride–ether (1:1) gave 3.69 g. of crude 2-methylene derivative, m.p. 167–174°, which was shown by thin layer chromatography to be partly contaminated with starting material. The crude product was subjected to a second purification by chromatography on 300 g. of Florisil. Elution with benzene–ether (9:1) and two recrystallizations from acetone afforded 1.02 g. of pure 17α-ethinyl-17-hydroxy-2-methyleneandrost-4-en-3-one as colorless plates, m.p. 182–184°, undepressed upon admixture with the sample prepared by method A. The infrared and n.m.r. spectra of this sample were identical with those of the sample prepared by method A.

Acknowledgment.—The authors are indebted to Dr. F. C. Nachod, Miss C. M. Martini, and Mr. M. Priznar for spectral determinations, and to Mr. K. D. Fleischer and staff for analytical services.

The Alkaloids of *Tabernanthe iboga*. IX.[1] The Structures of the Ibogaline Derivatives, Kisantine and Gabonine

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Six years ago we reported[2] the isolation of twelve alkaloids from *Tabernanthe iboga* Baillon and determined the structures of nine of them.[3] Of the remaining three bases, which had been obtained in very small amounts, kimvuline has been shown to be identical with iboxygaine[4] and now kisantine and gabonine are recognized to be oxidation products of ibogaline (I),[5] which contain the oxindole (II) and the *o*-acetamidoacetophenone (III) chromophores, respectively.

Kisantine (II) [$\lambda_{\max}$ mμ (ϵ), 213 (31,700), 268–270 (6270) and sh 296 (4710); $\nu_{\mathrm{C=O}}^{\mathrm{Nujol}}$ 1670 cm.$^{-1}$] has spectral properties in agreement for a 5,6-dimethoxyoxindole chromophore; *cf.* carapanaubine[6] or 5,6-dimethoxyoxindole itself [$\lambda_{\max}$ mμ (ϵ), 264 (7440) and sh 299 (3600); $\nu_{\mathrm{C=O}}^{\mathrm{Nujol}}$ 1710 and 1680 cm.$^{-1}$].[7] This conclusion is borne out in the p.m.r. spectrum[8] which showed the presence of a strong singlet peak at 3.9 (2-MeO), two singlet peaks at 7.1 and 6.56 (two uncoupled aromatic protons), a singlet at 9.1 (NH), and the characteristic set of peaks at *ca.* 1 p.p.m. for the CH_3 of the ethyl moiety.

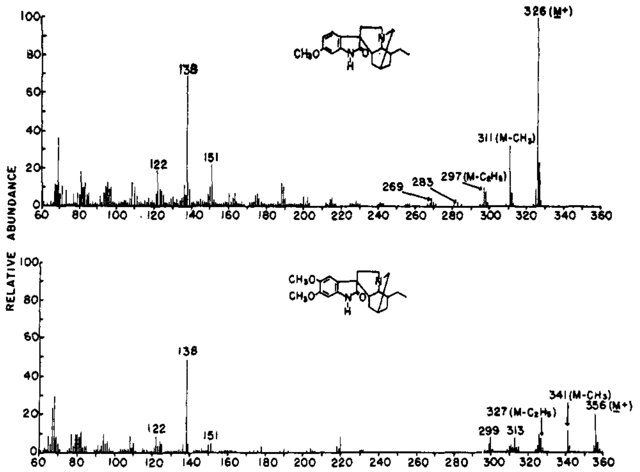
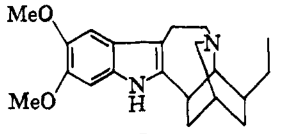
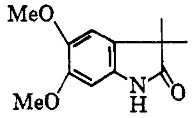


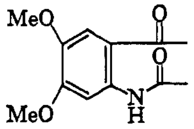
Figure 1.—Tabernanthine oxindole (above) and kisantine (II) (below).



I



II



III

Confirmation of these conclusions were obtained from a comparison of the mass spectra[9] of tabernanthine oxindole[8] and kisantine (Figure 1) which differ only in respect to those peaks which contain the extra methoxyl group.

Gabonine has an ultraviolet absorption spectrum [$\lambda_{\max}$ mμ (ϵ, calcd. for monomer), 250 (24,020), 283 (6620), and 348–350 (5530)] similar to that recorded for N-ethoxalyl-*o*-aminoacetophenone[10] and almost superimposable upon that of 2-acetamido-4,5-dimethoxybenzaldehyde [$\lambda_{\max}$ mμ (ϵ), 251 (35,200), 290 (9640), and 344 (7990)]. The p.m.r. spectrum[7] showed the expected singlet peaks at 10.15 (NH), 8.1 and 7.0 (the two aromatic protons), 3.95 and 3.90 (the two MeO), and the set of peaks *ca.* 1 p.p.m. (CH_3 of an ethyl group).

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(1) Part VIII. M. F. Bartlett, D. F. Dickel, R. C. Maxfield, L. E. Paszek, and A. F. Smith, *J. Am. Chem. Soc.*, **81**, 1932 (1959).

(2) D. F. Dickel, C. L. Holden, R. C. Maxfield, L. E. Paszek, and W. I. Taylor, *ibid.*, **80**, 123 (1958).

(3) M. F. Bartlett, D. F. Dickel, and W. I. Taylor, *ibid.*, **80**, 126 (1958).

(4) R. Goutarel, F. Percheron, and M.-M. Janot, *Compt. rend.*, **246**, 279 (1958). Iboxygaine (sample from M.-M. Janot) gives an undepressed mixture melting point and a superimposable infrared spectrum in Nujol with kimvuline.

(5) N. Neuss, *J. Org. Chem.*, **24**, 2047 (1959).

(6) B. Gilbert, J. A. Brissolese, N. Finch, W. I. Taylor, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *ibid.*, **85**, 1523 (1963).

(7) These and other simple oxindoles [G. N. Walker, *J. Am. Chem. Soc.*, **77**, 3845 (1955)] show two strong bands in the carbonyl region not shown by their 3,3-disubstituted derivatives, *e.g.*, the oxindole alkaloids; ref. 6 and N. Finch and W. I. Taylor, *ibid.*, **84**, 3871 (1962), and references therein.

(8) The p.m.r. spectra were run in deuteriochloroform on a Varian A-60 using tetramethylsilane as an internal standard. The shifts are reported in parts per million using the tetramethylsilane signal as reference.

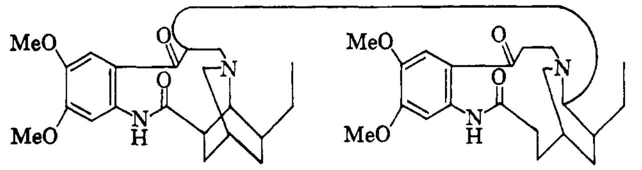
(9) The mass spectra were determined for us through the kindness of Dr. C. Djerassi.

(10) R. Goutarel, M.-M. Janot, V. Prelog, and W. I. Taylor, *Helv. Chim. Acta*, **33**, 150 (1950).

In the infrared spectrum gabonine had a set of peaks in Nujol at 1595, 1620, and 1672 cm.$^{-1}$ (broad) in good agreement with the model (1595, 1610, 1650, and 1680 cm.$^{-1}$).

An attempt was made to prove the validity of these conclusions by ring closure to a 4-quinolinol (*cf.* ring closure of the analogous yohimbine derivative[11]); the compound remained unchanged as also did the related ozonolysis product of voacangine.[12] A Dreiding model of the tetracyclic system (left-hand monomeric unit of IV) derived from ibogaline showed that the preferred configuration of the ten-membered ring was not favorable for ring closure (*cf.* an analogous situation for vobasine[13]). It may well be that the formation of iboquine by autooxidation of ibogaine does not proceed *via* a ring-opened intermediate.

When the mass spectrum of gabonine was run the molecular ion was found to be exactly twice what was expected, *viz.*, 2 × 372; hence, it is at least a dimer. The paucity of gabonine and the rareness of ibogaline makes the attempted preparation of the former from the latter impossible for the moment, and structure IV for gabonine is put forward as a working hypothesis only.



IV

In view of the known ease of autoöxidation of the iboga-class indoles,[2,3] the possibility exists that kinsantine and gabonine may be artefacts isolated instead of ibogaline, which we never detected.

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(11) B. Witkop and S. Goodwin, *J. Am. Chem. Soc.*, **75**, 3371 (1953).

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A Study of Anodic Acetoxylation Potentials[1]

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The Kolbe electrochemical reaction is usually considered[2,3,4a] to proceed according to the free-radical mechanism that is shown in the equation following,

$$2RCOO^- - 2e \longrightarrow 2RCOO\cdot \longrightarrow 2CO_2 + 2R \longrightarrow R_2 \qquad (1)$$

though attempts to make use of the Kolbe reaction for alkylation have not been particularly successful. Trinitrotoluene has been methylated to trinitroxylene[5] and pyridine alkylated to isomeric methylpyridines[6] and phenylpyridines,[7,8] all, however, in low yield. Several acyloxylations have also been reported, the acetoxylation of anisole,[9] furan,[9] and naphthalene.[10] These acyloxylations have been considered[2,3,9] to occur by attack of the acetoxy radical upon the substrate before decarboxylation could occur.

Our studies indicate, however, that, at least in the case of the formation of naphthyl acetate, the reaction probably does not proceed *via* the formation of an acetoxy radical which then adds to the naphthalene. Instead, the naphthalene molecule is first oxidized to a radical carbonium ion which then reacts further, according to the following scheme.

$$C_{10}H_8 - e \longrightarrow C_{10}H_8^+ \longrightarrow \text{products} \qquad (2)$$

Experimental

We first repeated the work of Linstead, *et al.*[10] They reported a 24% yield of α-naphthyl acetate, which, however, they did not isolate. They hydrolyzed and acidified the crude product and recovered the naphthol from the steam distillate. We looked for but were not able to detect any methylnaphthalenes in either the crude reaction mixture or the steam distillate, by column chromatography. We noted no anodic gas evolution, even at current densities up to 1 amp./cm.^{2}. Since the acetoxy radical is highly unstable[11,4b] either these radicals were not formed or they reacted before they could decompose. The half-life of the acetoxy radical is estimated[11] to be of the order of 10^{-9}–10^{-10} seconds and even if the electric field exerted a stabilizing influence, it is difficult to see how the naphthalene could react with all of the radicals before they could decompose.

We then investigated the electrochemical behavior of the naphthalene–acetic acid system and other related hydrocarbon–acetic acid systems. No attempt was made to isolate and determine the reaction products, which could not have been present in more than milligram quantities. No solution was electrolyzed long enough to consume more than about 0.1% of the organic reductant.

Current density–anode potential measurements were made in solutions of potassium acetate, ammonium acetate, and zinc chloride, in anhydrous acetic acid, with and without added benzene, anthracene, and naphthalene. Anode potentials were measured using an interrupter technique to eliminate ohmic drop. The current was interrupted with an electronic circuit for 20-μsec. intervals every millisecond and the potential was determined from the voltage–time trace on a calibrated oscilloscope. The current was measured from the potential fall across a resistor in series with the circuit.

The cathode was a silver plate coated with silver chloride to avoid the evolution of hydrogen. The anode was a 1.2-cm.^{2} piece of bright platinum. (Later results using platinized titanium agreed with those on platinum.) The reference electrode was a silver–silver chloride wire. All solutions were saturated with respect to KCl or $ZnCl_2$.

The cell was a 5 × 30 cm. Pyrex glass tube into which ground glass joints were sealed to admit the solution and to hold the three electrodes. The electrodes were sealed into the glass. The joints were fitted with Teflon sleeves to avoid the use of greases but were not completely airtight. However, the deliberate addition of enough water to a previously anhydrous solution to make it about 0.25 *M* with respect to water increased the potentials at

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(1) Work was performed at the City College of the City University of New York.

(2) B. C. L. Weedon, "Advances in Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 1–34.

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(8) P. J. Bunyan and D. H. Hey, *J. Chem. Soc.*, 3787 (1960).

(9) C. L. Wilson and W. T. Lippincott, *J. Electrochem. Soc.*, **103**, 672 (1956).

(10) R. P. Linstead, J. C. Lunt, B. C. L. Weedon, and B. R. Shephard, *J. Chem. Soc.*, 3624 (1952).

(11) W. Braun, L. Rajkenbuch, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).