459. *The Pyrolysis of Amine Oxides, and Hofmann Degradation, in the Benzylisoquinoline and Phthalideisoquinoline Series of Alkaloids.*

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The Hofmann degradation of hydroxylaudanosine, ketolaudanosine, narcotinediol, and hydrastinediol has been shown to result in fission of the molecule, and the same type of process has been observed on pyrolysis of β-hydroxylaudanosine *N*-oxide. Pyrolyses of the amine oxides of laudanosine, narcotine, and hydrastine follow a course analogous to the Hofmann degradation of these bases.

It was shown by King and L'Ecuyer [1] that the quaternary salts of the two isomers of hydroxylaudanosine (I) are degraded by Hofmann's method, not to the expected ketone (II), but to veratraldehyde (III) and the base (V). We have re-examined this degradation for β-hydroxylaudanosine, and have found no conditions of degradation under which this fission of the molecule is not observed. The proton most readily removed from the salt (I) is not either of those β to the nitrogen atom, but that of the hydroxyl group, as in (I). Where this hydroxyl group is bound in a lactone ring, as in narcotine,[2] or in a cyclic ether system,[3] then normal Hofmann degradation occurs, and this is the subsequent fate of the base (IV) produced by the fission of (I), the final product being the styrene (V). The whole process is governed by the ease of formation of the transitory ylid (IV), which is increased by the positive charge on the nitrogen atom; β-hydroxylaudanosine itself is recovered unchanged from refluxing methanolic potassium hydroxide.

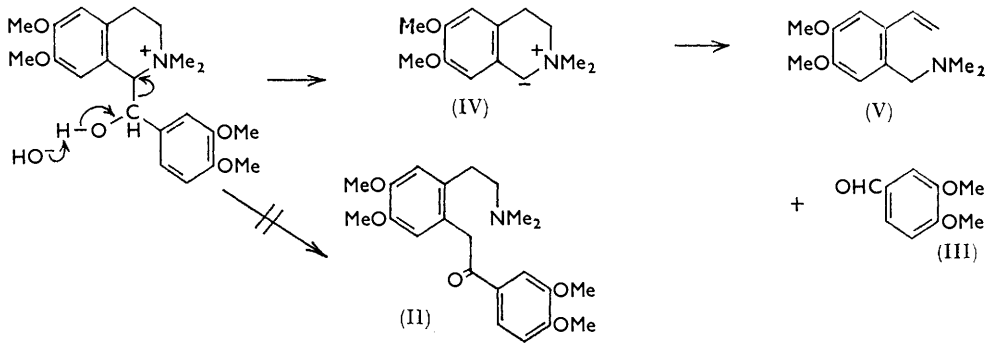
That this fission is a general process with compounds having a free hydroxyl group in the same position as in β-hydroxylaudanosine was demonstrated by the degradation of the diols (VI; R = OMe and H) obtained by the reduction of narcotine and hydrastine, respectively, with lithium aluminium hydride. These diols afforded the bases (VII; R = OMe and H) together with ψ-meconine (VIII). This lactone presumably arises either by Cannizzaro reaction or by autoxidation of the initially formed aldehyde.

The degradation of hydrastinediol (VI; R = H) gave a small amount of a basic

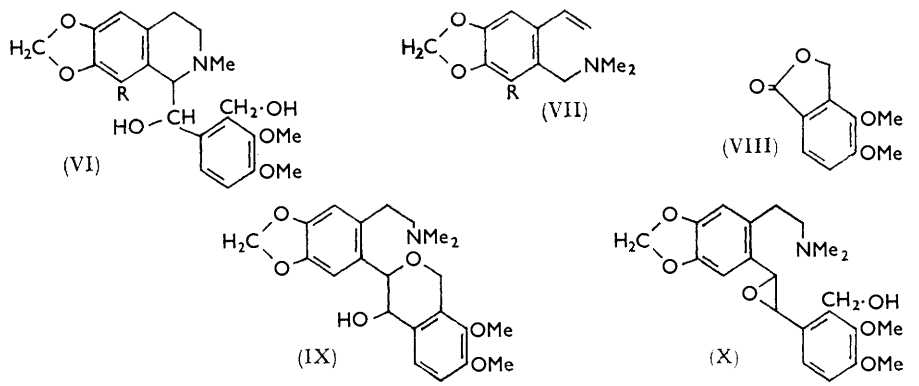
[1] King and L'Ecuyer, *J.*, 1937, 427.
[2] Hope and Robinson, *J.*, 1914, **105**, 2085.
[3] Bentley and Murray, preceding paper.

by-product formulated as (IX) or (X) by analogy with the Hofmann degradation product of ephedrine methohydroxide;[4] as expected the compound showed neither carbonyl nor styrenoid absorption in the infrared region. Insufficient was isolated for further investigation but its stability to cold hydrobromic acid indicates structure (IX); no analogous compound was formed from narcotinediol. Alkaline degradation of the methiodide of ketolaudanosine[3] also involves fission, to give veratric acid and the base (V).

In each of these three cases, the parent base was recovered unchanged after prolonged boiling with methanolic potassium hydroxide.



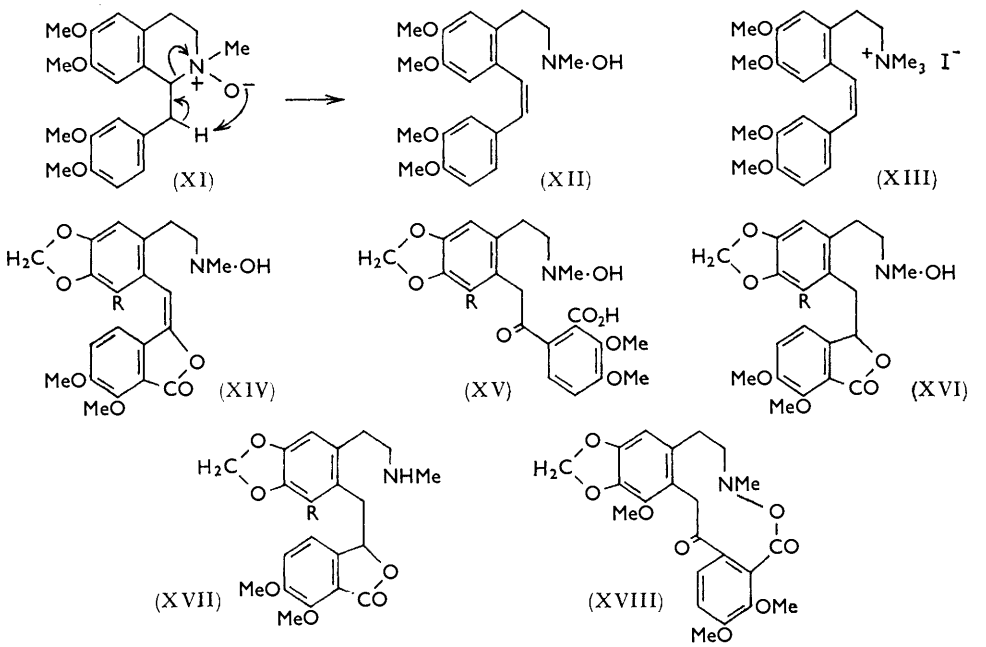
The pyrolytic degradation of tertiary amine oxides has so far been applied in the alkaloid field only to simple and complex derivatives of morphine and thebaine[5] in which the nitrogen atom is no longer part of a ring. In these cases remarkable success was achieved in preparing nitrogen-free products inaccessible by the more conventional Hofmann process. The application of this reaction to the compounds cited above which suffer abnormal Hofmann degradation was accordingly examined.



It has been established[6] that this process requires an intramolecular mechanism involving a planar quasi-five-membered cyclic transition state. Although steric factors therefore prevent degradation involving attack by the negative oxygen atom of the 4-hydrogen atom, the exocyclic β-hydrogen atom in the benzylisoquinoline series (analogous to the β-hydrogen atom attached to the carbon atom of the methyl group in *N*-methyl-α-pipecoline oxide which gives on pyrolysis a variable yield of *N*-hex-5-enyl-*N*-methylhydroxylamine[7]) may be accessible to intramolecular attack with formation of a stilbenoid double bond.

[4] Witkop and Foltz, *J. Amer. Chem. Soc.*, 1957, **79**, 197.
[5] Bentley, Ball, and Ringe, *J.*, 1956, 1963.
[6] Cram and McCarty, *J. Amer. Chem. Soc.*, 1954, **76**, 5740.
[7] Cope and Le Bel, *J. Amer. Chem. Soc.*, 1960, 4656.

Pyrolysis of laudanosine *N*-oxide (XI) gave the unstable stilbene (XII), identified by conversion into the methiodide (XIII) which was further degraded to the known nitrogen-free substance.[8] Narcotine *N*-oxide and hydrastine *N*-oxide likewise, when heated, suffered degradation to the enol-lactones (XIV; R = OMe and H, respectively). Acidic hydrolysis of these bases resulted in rupture of the enol-lactone systems and production



of the acids (XV; R = OMe and H, respectively). Catalytic hydrogenation of the lactone (XIV; R = OMe) in neutral solution over palladised strontium carbonate gave its dihydro-derivative (XVI; R = OMe); hydrogenation of the lactones in acetic acid over platinum oxide resulted in the absorption of 2 mol. of hydrogen and formation of the secondary bases (XVII; R = OMe and H).

The lactone (XIV; R = OMe) prepared from narcotine *N*-oxide is identical with the substance prepared by the Polonovskis [9] and assigned by them a quite different structure (XVIII). In support of our more plausible structure we cite, in addition to the conversion of the substance into the reduced bases (XVI and XVII; R = OMe), the fact that the infra-red spectrum of the base shows only one carbonyl absorption band, at 1770 cm.$^{-1}$, and this can be assigned to the phthalide system bearing the exocyclic unsaturation.[10]

Pyrolysis of β-hydroxylaudanosine *N*-oxide yielded tar from which only veratraldehyde could be isolated. This probably results from attack of the alcoholic hydroxyl group by the negative oxygen atom of the *N*-oxide, fission of the molecule occurring as in the cases of the Hofmann degradation (I) ⟶ (III); no products were isolated after thermal decomposition of the amine oxides of the diols (VI; R = OMe and H), but there is little doubt that these reactions proceed with fission in the same way.

Experimental

Reduction of Narcotine.—Narcotine (12 g.), dissolved in dry benzene (300 ml.), was gradually added to a stirred suspension of lithium aluminium hydride (1·5 g.) in benzene (100 ml.). The

[8] Decker and Galatty, *Ber.*, 1909, **42**, 1179.
[9] Polonovski and Polonovski, *Bull. Soc. chim. France*, 1930, **47**, 361.
[10] Grove and Wills, *J.*, 1951, 887.

mixture was then refluxed for 2 hr., cooled in an ice-bath, and the excess of reagent decomposed by dropwise addition of water, followed by 15% sodium hydroxide solution. The two phases were separated and the aqueous layer was saturated with salt and extracted with benzene. The solid diol (VI; R = OMe; 9·2 g.) resulting from evaporation of the dried benzene extracts crystallised from benzene–heptane as needles, m. p. 134° (lit.,[11] m. p. 134°) (Found: C, 63·1; H, 6·6; N, 3·5. Calc. for $C_{22}H_{27}NO_7$: C, 63·3; H, 6·5; N, 3·35%). The *methiodide*, obtained by heating the diol (2 g.) with methyl iodide (3 ml.) on a steam-bath for 2 hr., crystallised from ethanol as stout prisms (2·1 g.), m. p. 219—220·5°, sintering at 214° (Found: C, 49·2; H, 5·5. $C_{22}H_{27}NO_7,CH_3I$ requires C, 49·4; H, 5·5%).

Similarly, hydrastine (12 g.) was reduced to the corresponding diol (VI; R = H) (9·1 g.) which crystallised from benzene–heptane as opaque prisms, m. p. 143·5—144° (lit.,[11] m. p. 143—144°) (Found: C, 65·0; H, 6·6; N, 3·4. Calc. for $C_{21}H_{25}NO_6$: C, 65·1; H, 6·5; N, 3·6%). The *methiodide* crystallised from ethanol as prisms, m. p. 207—217·5° (Found: C, 50·0; H, 5·3. $C_{21}H_{25}NO_6,CHI_3$ requires C, 50·1; H, 5·3%).

Hofmann Degradation of Narcotine Diol (VI; R = OMe).—A solution of the methiodide (2 g.) in water (15 ml.) was boiled with 30% aqueous sodium hydroxide (20 ml.) for 2 hr. The liberated yellow oil was extracted with chloroform, and the dried extract was evaporated *in vacuo*. Distillation of the residual oil (0·8 g.) gave a small amount of NN-*dimethyl*-2-*methoxy*-3,4-*methylenedioxy*-6-*vinylbenzylamine*, b p. 158—160°/1 mm., which darkened on storage (Found: C, 65·9; H, 7·2; N, 5·6. $C_{13}H_{17}NO_3$ requires C, 66·4; H, 7·2; N, 5·9%), $\lambda_{max.}$ 288 mμ (log ε 3·83), $\nu_{max.}$ 913 cm.$^{-1}$ (vinyl group). The *picrate* formed yellow plates (from ethanol), m. p. 175—175·5° (Found: C, 49·2; H, 4·5; N, 11·8%. $C_{13}H_{17}NO_3,C_6H_3N_3O_7$ requires C, 49·1; H, 4·3; N, 12·1%). The *methiodide* separated from ethanol as prisms, m. p. 134—135° (Found: C, 44·9; H, 5·7. $C_{13}H_{17}NO_3,CH_3I$ requires C, 44·6; H, 5·4%).

Acidification of the residual alkaline solution with hydrochloric acid immediately afforded ψ-meconine, prisms (0·38 g.) (from ethanol), which sublimed at 100°, as needles, m. p. 123—124° (lit.,[12] m. p. 123—124°) (Found: C, 61·8; H, 5·3. Calc. for $C_{10}H_{10}O_4$: C, 61·9; H, 5·2%), $\nu_{max.}$ 1757 cm.$^{-1}$ (five-ring lactone).

Catalytic Reduction of NN-*Dimethyl*-2-*methoxy*-3,4-*methylenedioxy*-6-*vinylbenzylamine*.—A solution of the base (90 mg.) in ethanol (2 ml.), acidified with concentrated hydrochloric acid, was hydrogenated over palladium; ~1 mol. of hydrogen (8 ml.) was rapidly absorbed. The catalyst was removed, the solution was concentrated, and the resulting gum was dissolved in water and decomposed with sodium carbonate. The precipitated NN-*dimethyl*-6-*ethyl*-2-*methoxy*-3,4-*methylenedioxybenzylamine*, isolated by chloroform-extraction, had b. p. 132°/0·05 mm. (Found: C, 66·1; H, 7·9; N, 5·7. $C_{13}H_{19}NO_3$ requires C, 65·8; H, 8·0; N, 5·9%), $\lambda_{max.}$ 283 mμ (log ε 3·58).

Hofmann Degradation of Hydrastinediol (VI; R = H).—A solution of the methiodide (2 g.) in water (15 ml.) was boiled with 15% aqueous potassium hydroxide (20 ml.) for 2 hr. Ether-extraction and distillation gave: NN-*dimethyl*-4,5-*methylenedioxy*-2-*vinylbenzylamine* (0·75 g.), b. p. 110—111°/0·8 mm. (Found: C, 70·6; H, 7·0; N, 7·0. $C_{12}H_{15}NO_2$ requires C, 70·2; H, 7·3; N, 6·8%), $\lambda_{max.}$ 283 mμ (log ε 3·74), $\nu_{max.}$ 915 cm.$^{-1}$ (vinyl) [*methiodide*, irregular plates (from ethanol) subliming at 180° and decomposing just above this temperature (Found: C, 44·6; H, 5·0; I, 36·2. $C_{12}H_{15}NO_2,CH_3I$ requires C, 44·9; H, 5·2; I, 36·6%)]; and 3-[(2-*dimethylaminoethyl*)-4,5-*methylenedioxyphenyl*]-7,8-*dimethoxyisochroman*-4-*ol* (0·25 g.), b. p. 125—127°/0·3 mm. [*methiodide*, rectangular prisms, m. p. 249—250°, from 80% ethanol (Found: C, 50·6; H, 5·7; N, 2·5; I, 23·2. $C_{22}H_{27}NO_6,CH_3I$ requires C, 50·8; H, 5·5; N, 2·6; I, 23·4%), $\lambda_{max.}$ 276 mμ (log ε 4·21)]. Treatment of an aqueous solution of the last methiodide with an excess of aqueous sodium perchlorate precipitated, in 24 hr., the *methoperchlorate*, needles (from water), m. p. 212·5—213·5° (Found: C, 53·6; H, 5·8. $C_{22}H_{27}NO_6,CH_3ClO_4$ requires C, 53·5; H, 5·8%). The methiodide was unaffected by hydrobromic acid (no conversion into bromohydrin).

The alkaline mother-liquor from the Hofmann degradation afforded also ψ-meconine (0·25 g.) on acidification.

Hofmann Degradation of Ketolaudanosine.[3]—Ketolaudanosine methiodide (1 g.) was boiled for 2 hr. with 30% sodium hydroxide solution (15 ml.), and the products were isolated with

[11] Mirza and Robinson, *Nature*, 1950, **166**, 271
[12] Salomon, *Ber.*, 1887, **20**, 889.

chloroform. Removal of solvent and distillation of the residue gave *NN*-dimethyl-4,5-didimethoxy-2-vinylbenzylamine (0·41 g.), b. p. 126°/2 mm. (Found: C, 70·0; H, 8·4; N, 5·8. Calc. for $C_{13}H_{19}NO_2$: C, 70·6; H, 8·6; N, 6·3%). The picrate, crystallised from ethanol, sublimed before melting at 159—159·5° (lit.,[1] m. p. 158—159°) (Found: C, 50·7; H, 5·0; N, 12·3. Calc. for $C_{13}H_{19}NO_2,C_6H_3N_3O_7$: C, 50·7; H, 5·2; N, 12·5%). On treatment of the free base with an excess of methyl iodide an orange oil was formed, which solidified on gentle warming. The methiodide separated from ethanol as prisms, m. p. 197—198° (lit.,[1] m. p. 197—198°) (Found: C, 46·2; H, 6·2. Calc. for $C_{13}H_{19}NO_2,CH_3I$: C, 46·3; H, 6·3%).

Acidification of the extracted alkaline solution from the Hofmann degradation, produced needles (0·22 g.), m. p. 182° alone or mixed with veratric acid (Found: C, 59·1; H, 5·6. Calc. for $C_9H_{10}O_4$: C, 59·3; H, 5·5%), $\nu_{max.}$ 1680 cm.$^{-1}$ (aryl CO_2H).

Catalytic Reduction of NN-*Dimethyl-4,5-dimethoxy-2-vinylbenzylamine.*—A solution of the base (0·3 g.) in ethanol (5 ml.) containing concentrated hydrochloric acid (1 ml.) was hydrogenated over palladium chloride (0·1 g.); ~1 mol. was rapidly absorbed, and *NN*-dimethyl-2-ethyl-4,5-dimethoxybenzylamine was obtained as an oil, b. p. 126°/0·1 mm. (Found: C, 69·8; H, 9·1; N, 6·0. Calc. for $C_{13}H_{21}NO_2$: C, 70·0; H, 9·4; N, 6·3%).

Alkaline Treatment of the Parent Bases.—Each of the parent bases, β-hydroxylaudanosine, the narcotinediols (VI; R = OMe), hydrastinediol (VI; R = H), and ketolaudanosine, in 1·5-g. portions, was treated with 20% methanolic potassium hydroxide solution (20 ml.), and the mixtures were refluxed in an oil-bath for periods of up to 5 hr., then cooled and continuously extracted with chloroform; the extracts were dried and evaporated *in vacuo*. In each case the original base was recovered unchanged.

(±)-*Laudanosine* N-*Oxide.*—(±)-Laudanosine (3 g.), prepared by reduction of papaverine methosulphate[3] with sodium borohydride, was treated with 30% hydrogen peroxide (3 ml.) on a steam-bath until a yellow homogeneous solution was obtained. After treatment of the boiling solution with platinum wire, the solution was concentrated at 100° *in vacuo* to give the amine oxide as a brittle, hygroscopic, pale yellow foam. This was dissolved in water and treated with aqueous picric acid. The *picrate* was triturated with ethanol; it crystallised from acetone as stout yellow prisms, m. p. 172·5—174° (decomp.) after darkening at 167° (Found: C, 53·8; H, 5·1. $C_{21}H_{27}NO_5,C_6H_3N_3O_7$ requires C, 53·8; H, 4·9%), $\nu_{max.}$ (of *N*-oxide) 950 cm.$^{-1}$ (N–O).

Degradation of Laudanosine N-*Oxide.*—The impure *N*-oxide (2·5 g.) was heated gradually in an oil-bath at 0·1 mm. until decomposition began at 150°. After 10 min. at this temperature, the product was cooled, triturated with water and sodium carbonate solution, and extracted with chloroform. Washing, drying, and evaporation gave a brown varnish which decomposed on storage; neither methiodide nor picrate was obtained crystalline. An ethanolic solution of the base gave a deep red colour with alkaline triphenyltetrazolium chloride (Snow's test [13] for *N*-OH).

Reduction and Quaternisation of the Degradation Product (XII).—The crude product of pyrolysis of the amine oxide (2 g.), in the minimum of methanol, was heated with an excess of methyl iodide in a sealed tube for 5 hr. at 120°. Evaporation, and two crystallisations of the residue from aqueous ethanol, gave *laudanosinemethine methiodide* (1·5 g.) as needles, m. p. 233—234·5° (Found: C, 53·4; H, 6·1; I, 25·1. $C_{22}H_{29}NO_4,CH_3I$ requires C, 53·8; H, 6·2; I, 24·8%).

Hofmann Degradation of Laudanosinemethine Methiodide.—The methiodide (1·2 g.) was refluxed with 20% potassium hydroxide solution (15 ml.) until the odour of trimethylamine had disappeared (1½ hr.). The mixture was then cooled and extracted with ether. Drying and evaporation gave an oil which on crystallisation from ethanol (charcoal) gave the 3′,4,4′,5-tetramethoxy-2-vinylstilbene, m. p. 93—94°, previously prepared by two-stage exhaustive methylation of laudanosine [8] (Found: C, 73·4; H, 6·9. Calc. for $C_{20}H_{22}O_4$: C, 73·1; H, 6·8%).

Narcotine N-*Oxide.*—Attempts to prepare narcotine *N*-oxide by using 30% hydrogen peroxide resulted in decomposition (probably because these alkaloids contain easily oxidisable groups which are affected by hydrogen peroxide), and this oxide was eventually prepared by Polonovski and Polonovski's method; [9] it was obtained as a hygroscopic, pale yellow product (which decomposed on storage), giving a picrate, m. p. 128° (decomp.) [lit.,[9] m. p. 130° (decomp.)] (Found: N, 9·5. Calc. for $C_{22}H_{23}NO_8,C_6H_3N_3O_7$: N, 9·6%), and a hydrochloride, m. p. 190—191° (Found: C, 56·4; H, 5·3; Cl, 7·4. Calc. for $C_{22}H_{23}NO_8,HCl$: C, 56·7; H, 5·2; Cl, 7·6%), $\nu_{max.}$ (*N*-oxide) 950 cm.$^{-1}$ (N–O), 3400 cm.$^{-1}$ (OH).

[13] Snow, *J.*, 1954, 2588.

Degradation of Narcotine N-*Oxide*.—The *N*-oxide (4 g.) was heated at 0·1 mm. until decomposition occurred (115—120°). The tarry residue was worked up as above. Trituration with acetone of the yellow residue from chloroform extraction gave *anhydro*-N-*hydroxynornarceine* (1·8 g.), prisms (from acetone), m. p. 229° (Found: C, 61·2; H, 5·4; N, 2·9. $C_{22}H_{23}NO_8$ requires C, 61·1; H, 5·4; N, 3·3%), $\lambda_{max.}$ 322 mμ (log ε 3·89) and 345 mμ (log ε 3·83), $\nu_{max.}$ 1770 (unsaturated lactone), 3250 (bonded OH), and 930 cm.$^{-1}$ (enol–lactone double bond). The base immediately gave a deep red colour in Snow's test. The *hydrogen oxalate* crystallised from ethyl acetate as needles, m. p. 224·5—226° (Found: C, 55·8; H, 5·2. $C_{22}H_{23}NO_8,C_2H_2O_4$ requires C, 55·5; H, 4·8%).

Hydrolysis of Anhydro-N-*hydroxynornarceine*.—The preceding degradation product (0·5 g.) was dissolved in concentrated hydrochloric acid (5 ml.); after 6 hr. the precipitate was collected, washed with water, dissolved in dilute hydrochloric acid, and diluted with water. The precipitated N-*hydroxynornarceine* (0·2 g.) crystallised from aqueous ethanol as prisms, m. p. 191° (Found: C, 58·9; H, 5·9. $C_{22}H_{25}NO_9$ requires C, 59·1; H, 5·6%), $\lambda_{max.}$ 272 mμ (log ε 3·99), $\nu_{max.}$ 2500—2700 (bonded OH), 1680 (aryl acid), and 1730 cm.$^{-1}$ (aryl ketone).

Catalytic Reduction of Anhydro-N-*hydroxynornarceine*.—(*a*) *In neutral solution*. The base (0·8 g.) and palladised strontium carbonate (0·1 g.) in methanol (20 ml.) were shaken with hydrogen at room temperature and pressure (1 mol. absorbed). Filtration, evaporation, and sublimation at 200° gave the *dihydro-derivative* (XVI; R = OMe) (0·4 g.) as rectangular plates, m. p. 235—239·5° (Found: C, 61·6; H, 6·0; N, 3·4. $C_{22}H_{25}NO_8$ requires C, 61·3; H, 5·8; N, 3·2%), $\nu_{max.}$ 3250 cm.$^{-1}$ (bonded OH). Snow's test was positive. (*b*) *In acid solution*. The base (0·6 g.) and platinum oxide (0·1 g.) in glacial acetic acid (5 ml.) were shaken with hydrogen as before. Absorption was again slow, ceasing at two mol. Filtration and basification with ammonia gave the secondary *amine* (XVII; R = OMe) which crystallised from ethyl acetate as irregular flakes, m. p. 219° (decomp.) (Found: C, 63·4; H, 5·6. $C_{22}H_{25}NO_7$ requires C, 63·6; H, 6·0%), $\lambda_{max.}$ 302 mμ (log ε 3·65), $\nu_{max.}$ 3450 cm.$^{-1}$ (N–H); Snow's test was negative.

Hydrastine N-*Oxide*.—This was prepared as an unstable, hygroscopic paste by Polonovski and Polonovski's method.[9] The picrate formed yellow prisms (from ethanol), m. p. 128° (lit.,[9] m. p. 115°), which darkened on storage (Found: N, 8·7. Calc. for $C_{21}H_{21}NO_7,C_6H_3N_3O_7$: N, 8·9%), $\nu_{max.}$ 955 (N–O), 3400 cm.$^{-1}$ (OH).

Degradation of Hydrastine N-*Oxide*.—Decomposition of the oxide (4 g.) began at 140—145°/0·1 mm. and yielded an appreciable amount of dark polymer. Trituration with cold acetone of the oily, brown residue from chloroform-extraction slowly afforded the unsaturated *hydroxy-amine* (XIV; R = H) (1·7 g.), which crystallised from ethanol as yellow prisms, m. p. 187—187·5° (Found: C, 62·9; H, 5·3; N, 3·5. $C_{21}H_{21}NO_7$ requires C, 63·2; H, 5·3; N, 3·5%), $\lambda_{max.}$ 243 (infl.) (log ε 4·15), 325 (log ε 3·9), and 344 mμ (log ε 3·82), $\nu_{max.}$ 1770 [αβ,γδ(exocyclic)-unsaturated five-ring lactone], and 3250 cm.$^{-1}$ (bonded OH). The base gave a red colour with Snow's reagent. The *hydrogen oxalate* crystallised from alcohol as flakes, m. p. 194° to a dark red liquid (Found: C, 56·1; H, 4·6. $C_{21}H_{21}NO_7,C_2H_2O_4$ requires C, 56·4; H, 4·7%).

Hydrolysis of Compound (XIV; R = H).—The preceding product, being insoluble in concentrated acid, was hydrolysed by passing moist hydrogen chloride gas through a solution of the base (0·8 g.) in ethanol (10 ml.). The residue, after removal of solvent, was diluted with water and extracted with chloroform. Evaporation gave the *acid* (XV; R = H) (0·3 g.), prisms (from acetone–chloroform), m. p. 203—205° (Found: C, 60·8; H, 5·8. $C_{21}H_{23}NO_8$ requires C, 60·5; H, 5·5%), $\lambda_{max.}$ 274 mμ (log ε 3·98).

Catalytic Reduction of Compound (XIV; R = H).—Catalytic reduction in glacial acetic acid solution over platinum oxide was slow and ceased at 2 mol. The *product* (XVII; R = H) crystallised from ethanol as pale yellow nodules, m. p. 136—137° (Found: C, 65·3; H, 5·7. $C_{21}H_{23}NO_6$ requires C, 65·5; H, 6·0%).

β-*Hydroxylaudanosine* N-*Oxide*.—Attempts to prepare this amine oxide by the above methods failed; it was obtained as a sticky gum by adding a solution of the base (2 g.) in cold chloroform (10 ml.) to an ice-cold solution of perbenzoic acid (1 g.) in chloroform (15 ml.) and keeping the mixture overnight. The chloroform solution was then extracted with concentrated potassium hydroxide solution, dried, and evaporated to dryness *in vacuo*. The *N*-oxide was characterised as the *picrate*, needles (from water), m. p. 188—189° (decomp.) (Found: N, 8·7. $C_{21}H_{27}NO_6,C_6H_3N_3O_7,H_2O$ requires N, 8·8%).

Degradation of β-*Hydroxylaudanosine* N-*Oxide*.—Decomposition of the *N*-oxide (1 g.) at 140°/0·1 mm. afforded, after treatment with cold water and extraction with chloroform, a dark

resin. Distillation gave a very small fraction, b. p. 146°/11 mm., identified as veratraldehyde, m. p. and mixed m. p. 44—45° (Found: C, 65·4; H, 5·8. Calc. for $C_9H_{10}O_3$: C, 65·1; H, 6·1%), $\nu_{max.}$ 1670 cm.$^{-1}$ (aryl aldehyde). The 2,4-dinitrophenylhydrazone formed orange prisms (from ethyl acetate), m. p. 263—263·5° (Found: N, 16·2. Calc. for $C_{15}H_{14}N_4O_6$: N, 16·1%).

Attempted Degradation of the N-*Oxides of Narcotine- and Hydrastine-diol.*—Pyrolysis of the crude, uncharacterised amine oxides of the hydroxy-compounds (prepared by treatment of the parent bases with perbenzoic acid) resulted in complete decomposition (even at 100°/0·1 mm.) to intractable tars.

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