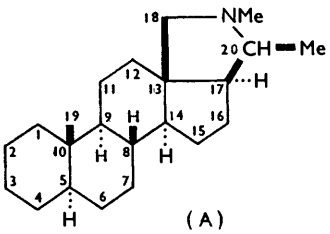
995. *The Constitution of Conessine. Part X.* Oxidation of Conessine and Pyrolysis of Some Oxidation Products.†*

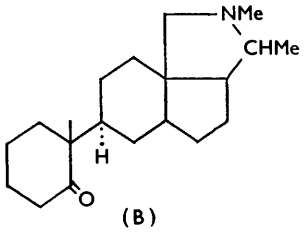
By R. D. Haworth and M. Michael.

The oxidation of conessine and its derivatives has been examined, and evidence favouring structures (II) and (VII) for "α-oxyconessine" and dioxyconessine respectively have been obtained. Oxidation and pyrolytic experiments along lines similar to those employed in steroid degradation have resulted in the preparation from conessine of derivatives in which (*a*) ring B is ruptured, (*b*) ring B is converted into a five-membered ring, and (*c*) rings A and B are removed leaving the C, D, and E rings of the alkaloid as a basic fragment (XXV) which may be approached by synthesis.

Nomenclature: As a result of consultations with the Editor the following method is adopted for the nomenclature of the conessine derivatives described in this communication.

The trivial name "conanine" is introduced for structure (A) and the assumption is made that conanine retains the stereochemistry of the alkaloid; the α-configuration assigned at position 5 is arbitrary as the alkaloid contains a 5 : 6-double bond. On this





basis conessine (I) and dioxyconessine (VII) would become 3β-dimethylaminocon-5-enine and 5 : 6-dihydroxy-3β-dimethylaminoconanine respectively. Application of the steroid rules (*J.*, 1951, 3526), using the *seco* and nor prefixes to indicate reductive bond rupture and ring contraction respectively, leads to 5-oxo-5 : 6-*seco*con-3-enin-6-oic acid, B-norcona-3 : 5-dienine, and 5-oxo-5 : 6-*seco*-B-norconanin-6-oic acid for (IX; R = H), (X), and (XXII; R = H) respectively.

Compounds (XIX) and (XXI) are regarded as hydroxymethylene and carbonyl derivatives of the parent structure (B) and, although it is unlikely that the steroid rules were intended to be used in such a complex way, they would lead to 5-oxo-5 : 8-*seco*-B-bisnorconanine for the parent (B) from which structures (XIX) and (XXI) become 4 : 8-hydroxymethylene- and 4 : 8-carbonyl-5-oxo-5 : 8-*seco*-B-bisnorconanine respectively.

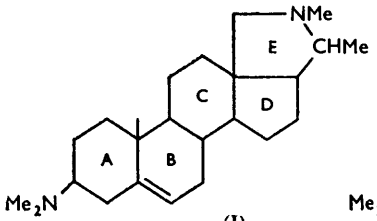
* Part IX, *J.*, 1956, 3749.

† In Part VIII (*J.*, 1955, 986) the $[\alpha]_D$ of 3α-acetamidocholest-5-ene is given as −53°, in reasonable agreement with Bannard and McKay's (*Canad. J. Chem.*, 1955, **33**, 1166) value of −59°, but not with the figures of −30° and −32° given by Shoppee and his collaborators (*J.*, 1955, 694; 1956, 1054). To support a criticism of Bannard and McKay's product, however, Shoppee, Evans, Richards, and Summers (*J.*, 1956, 1649) misquote us as having given in Part VIII the value $[\alpha]_D$ −31°.

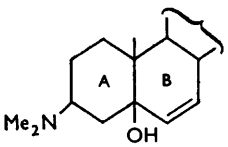
For the nomenclature of the tricyclic ring (XXIV) we propose to use the system employed by Sir Robert Robinson (*J.*, 1952, 1224) in which des-A-cholestane is used for cholestane stripped of the four methylene groups of ring A but retaining the rest of the original asymmetry. Thus (XXIV; R = Me) and (XXIV; R = H) become des-AB-con-8-enine, and de-*N*-methyl-des-AB-con-8-enine respectively.

For some of the products recorded below, configurations cannot be completely assigned. Bonds have therefore been denoted by " ordinary " lines rather than in accordance with the steroid conventions; names, however, are derived from conanine without stereochemical modifications.

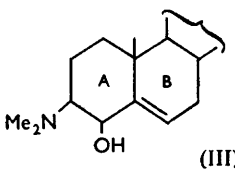
In order to obtain additional constitutional information the behaviour of the steroidal alkaloid conessine (I) towards oxidising agents has been examined. The action of ozone is complex and results in the formation of formaldehyde and water-soluble amorphous products.[1] Oxidation of conessine with selenium dioxide in water yielded Bertho's α-oxyconessine,[1] which probably possesses the 3β-dimethylamino-5-hydroxycon-6-enine structure



(I)

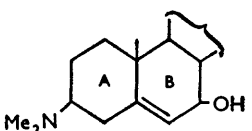


(II)



(III)

(II) in preference to either of the expected structures (III) or (IV). During attempted oxidation of this compound it was discovered that when treated with hydrogen peroxide in acid solution it readily gave 3β-dimethylaminocona-4 : 6-diene (V), which had been obtained previously by the action of phosphorus oxychloride on a benzene solution of α-oxyconessine by Bertho [2] who however characterised the anhydro-derivative (V) as the dihydriodide but failed to obtain the crystalline base. The ultraviolet absorption spectra of the anhydro-derivative (V) indicated a trisubstituted diene with the conjugation distributed between two rings as in structure (V). This structure (V) could arise from structures (III) or (IV) by 1 : 4-dehydration or from structure (II) by 1 : 2-dehydration, and the latter structure is preferred because we were unable to convert α-oxyconessine into a ketone by oxidation by the Oppenauer procedure or with cold chromic acid. Such a structure (II) probably arises from the isomer (IV) by allylic rearrangement similar to that involved in the conversion of cholest-5-ene-3β : 4β-diol into cholest-4-ene-3β : 6β-diol.[3]



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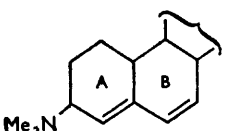
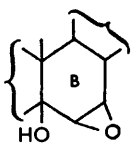


(V)



(VI)

Besides yielding the anhydro-derivative (V) the peroxide oxidation of 3β-dimethylamino-5-hydroxycon-6-enine (II) also gave a compound, $C_{24}H_{40}O_2N_2$, m. p. 225—226° (decomp.), which is possibly one of the diastereoisomeric forms of the epoxide (VI); and a second, isomeric epoxide, m. p. 163—164°, was obtained by oxidising 3β-dimethylamino-5-hydroxycon-6-enine with cold chromic acid. Attempts to convert the epoxides into triols were

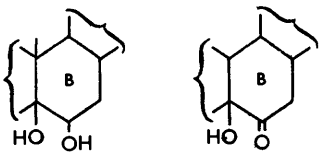
[1] Bertho, *Annalen*, 1947, **557**, 220.
[2] *Idem*, *ibid.*, 1951, **573**, 210.
[3] Rosenheim and Starling, *J.*, 1937, 377; Butenandt and Hausmann, *Ber.*, 1937, **70**, 1154.

unsuccessful and the oxidation of 3β-dimethylamino-5-hydroxycon-6-enine to such epoxides must be regarded as only provisional, as stable epoxides have rarely been isolated by direct oxidation of ethylenes except in the cases of tetrasubstituted derivatives.[4] The isolation of the epoxide, m. p. 163—164°, together with other unidentified products by oxidation of 3β-dimethylamino-5-hydroxycon-6-enine with hot chromic acid is noteworthy in this connection.

The oxidation of conessine with selenium dioxide has been examined with dioxan, pyridine, and " methyl cellosovle " (2-methoxyethanol) as solvent. Another isomeric base, $C_{24}H_{40}O_2N_2$, characterised as a crystalline picrate, and a base, $C_{24}H_{38}O_2N_2$, m. p. 240°, were isolated, but in small yields which prevented thorough investigation.

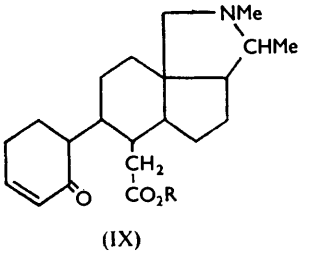
The conversion into 5-acetoxy-3β-dimethylaminocon-6-enine does not involve anionotropic change, as hydrolysis leads to the recovery of 3β-dimethylamino-5-hydroxycon-6-enine. The acetyl derivative was not attacked by iodic acid, but osmium tetroxide gave a product which after hydrolysis yielded still another isomer, $C_{20}H_{40}O_2N_2$, m. p. 240°, of unknown constitution. With potassium permanganate in acetone 5-acetoxy-3β-dimethylaminocon-6-enine gave a poor yield of an oily base which gave a crystalline monomethiodide, indicating that the basicity of one tertiary amino-group has been destroyed either by oxidation of an *N*-methyl to an *N*-formyl group or by oxidation of an $\rangle N{\cdot}CH_2{\cdot}$ to an $\rangle N{\cdot}CO{\cdot}$ group.

Some properties bearing on the constitution of dioxyconessine (3β-dimethylamino-5 : 6-dihydroxyconanine) were described in Part IV of this series,[5] and evidence in favour of structure (VII) has now been obtained by oxidation with cold chromic acid to 3β-dimethylamino-5-hydroxy-6-oxoconanine (VIII). Although it failed to yield hydroxyl or ketonic derivatives, when heated with formic acid 3β-dimethylamino-5-hydroxy-6-oxoconanine



(VII)

(VIII)

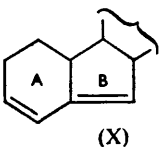


(IX)

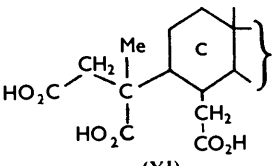
(VIII) gave a mixture of an isomer and another base produced by elimination of dimethylamine. The infrared spectrum of the product (VIII) indicated the presence of a hydroxyl group (3382 cm.$^{-1}$) and a six-membered ring ketone (1698 cm.$^{-1}$). It is also satisfactory that the *OO*-diacetyl derivative of 3β-dimethylamino-5 : 6-dihydroxyconanine, previously described by Giemsa and Halberkann [6] as a varnish, has now been obtained as a crystalline hydrate. Oxidative fission of ring B of 3β-dimethylamino-5 : 6-dihydroxyconanine (VII) was effected with hot chromic acid. This gave dimethylamine and a water-soluble amino-acid mixture from which 5-oxo-5 : 6-*seco*con-3-enin-6-oic acid (IX; R = H) was isolated, and the αβ-unsaturated ketonic structure was supported by the ultraviolet absorption spectra of the acid and its ethyl ester (IX; R = Et). Ring (B) of the alkaloid having been ruptured, it became of interest to determine appropriate conditions for the additional removal of ring (A), and the elegant methods used by Cornforth, Hunter, and Popják [7] in the degradation of cholesterol stimulated the remaining approaches described in this communication. Pyrolysis of the acid (IX; R = H) gave a basic mixture from which the

[4] Petrow, *J.*, 1939, 998; Ruzicka and Bossard, *Helv. Chim. Acta*, 1937, **20**, 244; Petrow and Starling, *J.*, 1940, 60.
[5] Haworth, McKenna, and Whitfield, *J.*, 1953, 1102.
[6] Giemsa and Halberkann, *Arch. Pharm.*, 1918, **256**, 201.
[7] Cornforth, Hunter, and Popják, *Biochem. J.*, 1953, **54**, 590.

main fraction, isolated by chromatography, was an oil yielding a crystalline methiodide. The ultraviolet spectrum of the oily base was consistent with the trisubstituted hetero-annular diene structure of B-norcona-3 : 5-dienine (X). When the amino-acid mixture containing 5-oxo-5 : 6-*seco*con-3-enin-6-oic acid (IX; R = H) was pyrolysed, a small



(X)



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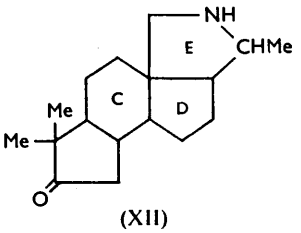
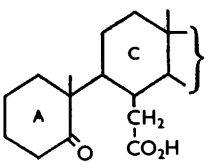


(XII)

amount of a crystalline base, $C_{17}H_{27}ON$, was isolated. Its infrared spectrum indicated the presence of an imino-group (3436 cm.$^{-1}$) and a five-membered ring ketone (1738 cm.$^{-1}$), and the presence of these groups was confirmed by the formation of a nitrosamine and a semicarbazone respectively. Structure (XII), arising from the undetected amino-tricarboxylic acid (XI), is provisionally suggested for the ketonic base, $C_{17}H_{27}ON$.

Hydrogenation of the diene (X) could be interrupted at the dihydro-stage, and the product was an oil, yielding a crystalline methiodide. This new oily base lacked the characteristic diene absorption, but residual unsaturation was shown by the ready liberation of iodine from iodic acid as in the conversion of conessine into dioxyconessine. However, as crystalline oxidation products were not obtained either from this reaction with iodic acid or from the action of permanganate in acetone, it was not possible to determine the constitution of the dihydro-product or even to establish its homogeneity. The preparation of a dihydro-derivative of (X) was, however, achieved in another way. Reduction of the amino-acid mixture obtained by oxidation of dioxyconessine with hot chromic acid yielded a mixture, presumably containing 5-oxo-5 : 6-*seco*conanin-6-oic acid (XIII), which on pyrolysis lost water and carbon dioxide and gave the crystalline unsaturated base B-norcon-5-enine (XIV) which was dimorphous and yielded a crystalline methiodide. The hydrochloride, prepared with ethereal hydrogen chloride, was also crystalline, but it was converted by warming with dilute hydrochloric acid into an isomeric hydrochloride which gave a new unsaturated base. This isomerism is possibly due to double-bond migration leading to B-norcon-8(9)-enine (XV) which would account for (*a*) the ready liberation of iodine shown with iodic acid and (*b*) the resistance shown by the new base to reduction by hydrogen in presence of a platinic oxide catalyst.



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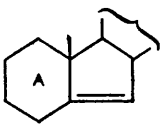

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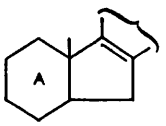
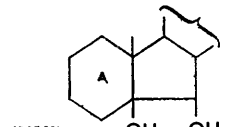


(XV)

An examination has also been made of the behaviour of B-norcon-5-enine (XIV) towards a number of oxidising agents. Iodic acid, hydrogen peroxide in acid solution, and chromic acid gave intractable gums, and ozonolysis followed by catalytic reduction of the ozonide gave non-basic amorphous material, probably by oxidation of the *N*-methyl group or the α-methylene group as well as attack at the double bond (see analogous behaviour in the annotonine series [8]). However, pyrolysis of the crude ozonolysis product resulted in the

[8] Betts and MacLean, *Canad. J. Chem.*, 1957, **35**, 211.

formation of 2-methyl*cyclo*hexanone, and a higher-boiling non-basic material, which unfortunately rapidly darkened and could not be investigated further. Potassium periodate, recently advocated as a reagent for double bonds,[9] reacted with the base (XIV)



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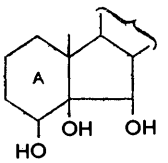
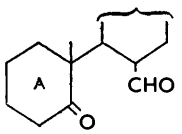


(XVII)

to give poor yields of 5 : 6-dihydroxy-B-norconanine (XVI), and a triol, possibly 4 : 5 : 6-trihydroxy-B-norconanine (XVII). It has been suggested [9,10] that periodate reacts *via* the epoxide and, since epoxides on fission give *trans*-diols,[11] a 5 : 6-*trans*-diol structure is favoured for (XVI); this diol certainly differs from the isomeric 5 : 6-*cis*-diol described below. The structure assigned to the triol (XVII) is based on the assumption that this compound arises from the diol (XVI) by dehydration and subsequent hydroxylation; if this is so, and if the hydroxylation proceeds by way of an epoxide which is cleaved to give two axial hydroxyl groups, then the triol (XVII) is a 4β : 5α : 6ξ-triol.

The 5 : 6-*cis*-diol (XVI), mentioned above, was obtained by the action of osmium tetroxide on B-norcon-5-enine (XIV). Reaction of this *cis*-diol with periodate gave, not the expected 5 : 6-dioxo-5 : 6-*seco*-B-norconanine (XVIII), but the isomeric 4 : 8-hydroxymethylene-5-oxo-5 : 8-*seco*-B-bisnorconanine (XIX) which formed a monosemicarbazone and whose infrared spectrum showed the presence of a hydroxyl group (3345 cm.$^{-1}$) and a six-membered ring ketone (1700 cm.$^{-1}$). Bredt's rule provides an explanation of the failure to convert the aldol (XIX) into an αβ-unsaturated ketone, and several cases of analogous aldol formation have been reported by Julia *et al.*[12] and by Prelog and Osgan.[13] When the aldol base (XIX) was treated with alkali in an attempt to induce a reversed aldolisation to 5 : 6-dioxo-5 : 6-*seco*-B-norconanine (XVIII), it was converted into 5-hydroxy-5 : 6-*seco*-B-norconanin-6-oic 5 : 6-lactone (XX), which is probably formed by dismut-



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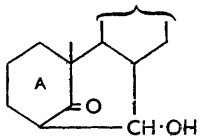
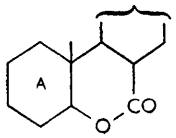


(XIX)

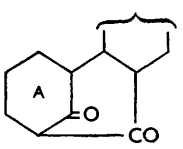


(XX)

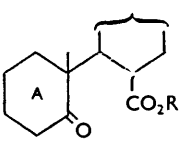
ation of the keto-aldehyde (XVIII) as observed by Cornforth, Gore, and Popják [14] in an analogous case. Direct pyrolysis of 4 : 8-hydroxymethylene-5-oxo-5 : 8-*seco*-B-bisnorconanine (XIX) gave 2-methyl*cyclo*hexanone and a small basic fraction from which a crystalline picrate was isolated, but in quantities insufficient for characterisation. Careful oxidation of the aldol (XIX) with chromic acid in cold acetic acid gave the β-diketone, 4 : 8-carbonyl-5-oxo-5 : 8-*seco*-B-bisnorconanine (XXI), which on alkaline hydrolysis underwent cleavage to 5-oxo-5 : 6-*seco*-B-norconanin-6-oic acid (XXII; R = H), which was characterised as its crystalline methyl ester. The direction of alkaline cleavage of the β-diketone (XXI) was established by direct oxidation of 5 : 6-*cis*-dihydroxy-B-norconanine

[9] Chatterjee and Majumdar, *Analyt. Chem.*, 1956, **28**, 878.
[10] Graber, Snoddy, Arnold, and Wendler, *J. Org. Chem.*, 1956, **21**, 1518.
[11] Winstein and Henderson in " Heterocyclic Compounds," Ed. Elderfield, Wiley, New York, 1950, Vol. I, p. 27.
[12] Julia, Eschenmoser, Heusser, and Tarkoy, *Helv. Chim. Acta*, 1953, **36**, 1888.
[13] Prelog and Osgan, *ibid.*, 1952, **35**, 981.
[14] Cornforth, Gore, and Popják, *Biochem. J.*, 1957, **65**, 94.

(XVI) in small yield to the same amino-acid (XXII; R = H). Pyrolysis of methyl 5-oxo-5 : 6-*seco*-B-norconanin-6-oate (XXII; R = Me) yielded the enol-lactone, 5-hydroxy-5 : 6-*seco*-B-norcon-4-enin-6-oic 5 : 6-lactone (XXIII), which was characterised as the methiodide. When, however, an intimate mixture of 5-oxo-5 : 6-*seco*-B-norconanin-6-oic acid (XXII; R = H) and potassium carbonate was pyrolysed, decarboxylation and the reverse Michael fission, utilised so freely in steroid degradations,[7,12,14,15] took place with the formation of 2-methyl*cyclo*hexanone and a basic fraction which was separated by chromatography into the two bases, des-AB-con-8-enine (XXIV; R = Me) and de-*N*-methyl-



(XXI)



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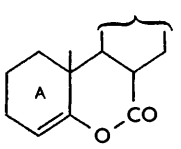
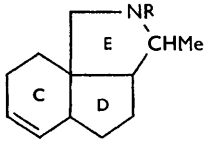


(XXIII)



(XXIV)

des-AB-con-8-enine (XXIV; R = H). The tertiary base (XXIV; R = Me) was an oil which gave a crystalline picrate; the secondary base (XXIV; R = H) was also an oil but gave an oily nitrosamine, showing a positive Liebermann test, and yielded a crystalline picrate. Catalytic reduction of des-AB-con-8-enine (XXIV; R = Me) gave a dihydro-derivative, des-AB-conanine, as an oil from which a crystalline picrate was prepared.

At this stage the quantities of the bases (XXIV; R = Me and H) were insufficient for further characterisation or for further degradation, and consequently experiments have been commenced which aim at the synthesis of these rather inaccessible compounds.

Experimental

Light petroleum refers to the fraction of b. p. 40—60°. Ultraviolet absorption spectra were measured for 95% ethanol solutions, and infrared absorption spectra with potassium bromide discs.

Oxidation of Conessine with Selenium Dioxide in Hot Water.—This reaction, carried out as described by Bertho,[1] gave 3β-dimethylamino-5-hydroxycon-6-enine (II), m. p. 158° (Found: C, 77·4; H, 11·1; N, 7·8. Calc. for $C_{24}H_{40}ON_2$: C, 77·4; H, 10·8; N, 7·5%). The infrared spectrum had *inter al.* a band at 3382 cm.$^{-1}$. 5-Acetoxy-3β-dimethylaminocon-6-enine, prepared according to Bertho,[16] was a pale yellow oil which slowly solidified and crystallised from aqueous acetone in colourless needles, m. p. 128° (Found: C, 75·2; H, 10·5; N, 6·9. Calc. for $C_{26}H_{42}O_2N_2$: C, 75·3; H, 10·2; N, 6·8%). Hydrolysis with N-methanolic potassium hydroxide gave 3β-dimethylamino-5-hydroxycon-6-enine, m. p. 158°. 3β-Dimethylamino-5-hydroxycon-6-enine was recovered after being refluxed with aluminium *iso*propoxide or *tert.*-butoxide in a mixture of toluene and *cyclo*hexanone.

Oxidation of 3β-Dimethylamino-5-hydroxycon-6-enine (II) *with Cold Chromic Acid.*—To a solution of 3β-dimethylamino-5-hydroxycon-6-enine (250 mg.) in acetic acid (20 ml.) was added a solution of chromium trioxide (90 mg.) in water (1·5 ml.) and acetic acid (4·5 ml.). After 87 hr. the solution was made alkaline by addition of sodium hydroxide, and the *epoxide*, isolated with ether, was a gum (230 mg.) which slowly solidified under light petroleum and separated from acetone in needles, m. p. 163—164° (Found: C, 74·0; H, 10·5; N, 7·1. $C_{24}H_{40}O_2N_2$ requires C, 74·2; H, 10·4; N, 7·2%), which were unaffected by boiling dilute sulphuric acid or by potassium hydroxide in boiling aqueous ethanol or aqueous dioxan.

Action of Hydrogen Peroxide on 3β-Dimethylamino-5-hydroxycon-6-enine.—3β-Dimethylamino-5-hydroxycon-6-enine (100 mg.), 2N-sulphuric acid (2·5 ml.), and 30% hydrogen peroxide

[15] Achtermann, *Z. physiol. Chem.*, 1934, **225**, 141; Laucht, *ibid.*, 1935, **237**, 236; Turner, *J. Amer. Chem. Soc.*, 1950, **72**, 579; 1954, **76**, 1390; Rinikier, Arigoni, and Jeger, *Helv. Chim. Acta*, 1954, **37**, 547.

[16] Bertho, *Annalen*, 1950, **569**, 1.

(0·15 ml.) were heated on the water-bath for 3 hr. Excess of peroxide was destroyed with sulphur dioxide, and the solution basified and extracted three times with ether. Removal of the solvent gave a gummy *epoxide* (85 mg.) which crystallised from acetone in colourless prisms (21 mg.), m. p. 225—226° (Found: C, 74·1; H, 10·4; N, 7·0. $C_{24}H_{40}O_2N_2$ requires C, 74·2; H, 10·4; N, 7·2%). The acetone mother-liquors were evaporated, and the residue was taken up in light petroleum and chromatographed on alumina (2 g.). Elution with light petroleum–ether (1 : 1) gave an oil which slowly solidified and was crystallised from aqueous acetone. 3β-*Dimethylaminocona*-4 : 6-*dienine* (V) (28 mg.) was obtained as colourless needles, m. p. 116° (Found: C, 81·7; H, 11·0; N, 8·0. $C_{24}H_{38}N_2$ requires C, 81·4; H, 10·7; N, 7·9%) undepressed on admixture with the product, m. p. 116°, of the action of phosphorus oxychloride on 3β-dimethylamino-5-hydroxycon-6-enine.[2] The diene had ultraviolet absorption max. at 2320, 2390, 2470 Å (infl.) (log ε 4·3, 4·35, 4·2).

Oxidation of Conessine with Selenium Dioxide in Dioxan.—Conessine (500 mg.) in pure dioxan (10 ml.) was refluxed with selenium dioxide (780 mg.) for 3 hr. The solvent was removed, water was added to the residue, and the selenium removed at a centrifuge. Basification of the aqueous layer and extraction with ether gave a gum (180 mg.), which was taken up in benzene and chromatographed on alumina (5 g.). Elution with more benzene gave crystals (60 mg.), m. p. 175—180°, recrystallising from *cyclo*hexane in colourless needles, m. p. 179—180°, which gave inconsistent analytical results but yielded a *picrate* separating from acetone in yellow needles, m. p. 110° (Found: C, 58·1; H, 7·2. $C_{24}H_{40}O_2N_2,C_6H_3O_7N_3$ requires C, 58·3; H, 7·0%).

Elution with chloroform yielded a *base* (27 mg.), m. p. 235—238°, which separated from benzene–light petroleum in colourless prisms, m. p. 240° (Found: C, 74·5; H, 9·9; N, 7·2. $C_{24}H_{38}O_2N_2$ requires C, 74·5; H, 9·9; N, 7·3%).

Similar results were obtained in pyridine or " methyl cellosolve."

Oxidation of 5-*Acetoxy*-3β-*dimethylaminocon*-6-*enine with Osmium Tetroxide.*—This acetate (1 g.) and osmium tetroxide (1 g.) in dry ether (100 ml.) were allowed to react at room temperature for 16 days. After evaporation of solvent the residue was shaken overnight with mannitol (5 g.) and N-potassium hydroxide (20 ml.). The alkaline solution was extracted three times with ether, the extracts were combined, and the solvent was removed. The residue (690 mg.) was divided into two parts and treated as follows:

(*a*) The gum (303 mg.) was refluxed with N-methanolic potassium hydroxide (10 ml.) for 1 hr. The methanol was removed, water added, and the product, isolated with ether, chromatographed on alumina (8 g.). Elution with ether gave 3β-dimethylamino-5-hydroxycon-6-enine (II) (82 mg.), m. p. and mixed m. p. 158°, and elution with ether–chloroform (1 : 1) yielded an oily *base* (110 mg.) which slowly crystallised and had m. p. 230—236°. Recrystallisation from *cyclo*hexane gave colourless needles, m. p. 239—241° (Found: C, 74·0; H, 10·0. $C_{24}H_{40}O_2N_2$ requires C, 74·2; H, 10·4%).

(*b*) The gum (276 mg.) was treated on the steam-bath with N-sulphuric acid (10 ml.) for 2 hr. After basification, the product was isolated with ether and chromatographed on alumina (8 g.), giving 3β-dimethylaminocona-4 : 6-dienine (V) (90 mg.), m. p. 116°, and a substance (38 mg.) which separated from *cyclo*hexane in colourless needles, m. p. 180°, which was not analysed.

Oxidation of 5-*Acetoxy*-3β-*dimethylaminocon*-6-*enine with Potassium Permanganate.*—A solution of potassium permanganate (420 mg.) in acetone (70 ml.) was added with shaking to a solution of 5-acetoxy-3β-dimethylaminocon-6-enine (410 mg.) in acetone (70 ml.). After 12 hr. at room temperature, the manganese dioxide was collected and washed with acetone, and the combined washings and filtrate were evaporated. The residue was taken up in ether, washed with dilute aqueous sodium hydroxide, and dried and the solvent removed. The residual gum (337 mg.) was chromatographed in ether–light petroleum (1 : 1) on alumina (9 g.), and separated into 5-acetoxy-3β-dimethylaminocon-6-enine (210 mg.), m. p. 128°, and an oil which gave a *monomethiodide* as colourless plates (from acetone), m. p. 234—235° (Found: C, 54·7; H, 7·8; N, 4·85. $C_{27}H_{43}O_3N_2I,H_2O$ requires C, 55·1; H, 7·7; N, 4·8%).

Dioxyconessine (3β-*Dimethylamino*-5 : 6-*dihydroxyconanine*).—The method of preparation described by Bertho [1] was more convenient than Warnecke's method [17] for the preparation of large quantities. The infrared spectrum had, *inter al.*, bands at 3382 and 3143 cm.$^{-1}$.

5 : 6-*Diacetoxy*-3β-*dimethylaminoconanine*.—3β-Dimethylamino-5 : 6-dihydroxyconanine (200

[17] Warnecke, *Arch. Pharm.*, 1888, **226**, 248.

mg.), pyridine (4 ml.), and acetic anhydride (1 ml.) were heated for 2 hr. on the steam-bath. Evaporation under reduced pressure and addition of water (1 ml.) gave an oil which crystallised during two days in a vacuum-desiccator over sulphuric acid. Recrystallisation from acetone gave 5 : 6-*diacetoxy*-3β-*dimethylaminoconanine monoacetate* as colourless needles, m. p. 194—196° (decomp.) (preheated bath) (Found: C, 67·8; H, 9·3; N, 5·2. $C_{28}H_{46}O_4N_2,CH_3{\cdot}CO_2H$ requires C, 67·4; H, 9·4; N, 5·2%). 5 : 6-Diacetoxy-3β-dimethylaminoconanine was prepared by dissolving this salt in dilute hydrochloric acid and basifying the solution with dilute sodium hydroxide; the base was collected, washed with a little water, dried, and crystallised from aqueous methanol; the *hydrate* separated as small needles (Found: C, 68·2; H, 10·3. $C_{28}H_{46}O_4N_2,H_2O$ requires C, 68·2; H, 9·9%) which when heated in a m. p. tube lost water and collapsed to a resin, m. p. 130—135°. The *methiodide*, prepared in acetone, separated from methanol in stout prisms, m. p. 296° (decomp.) (Found: C, 46·5; H, 7·2; N, 3·8. $C_{28}H_{46}O_4N_2,2CH_3I,H_2O$ requires C, 46·4; H, 7·0; N, 3·6%). Attempted partial hydrolysis of 5 : 6-diacetoxy-3β-dimethylaminoconanine hydrate was unsuccessful.

Oxidation of Dioxyconessine with Cold Chromic Acid.—A solution of chromium trioxide (200 mg.) in water (2·5 ml.) and acetic acid (7·5 ml.) was added to dioxyconessine (585 mg.) in acetic acid (40 ml.). After 72 hr. at room temperature, excess of oxidising agent was destroyed by addition of methanol (5 ml.), and the basified solution was continuously extracted with chloroform for 12 hr. Removal of the chloroform gave 3β-*dimethylamino*-5-*hydroxy*-6-*oxoconanine* (VIII) which separated from ethanol in stout needles, m. p. 281—282° (Found: C, 73·8, 74·2; H, 10·5, 10·6; N, 7·2, 7·2. $C_{24}H_{40}O_2N_2$ requires C, 74·2; H, 10·4; N, 7·2%), which sublimed at 180°/10 mm. The infrared spectrum had, *inter al.*, bands at 3382 and 1698 cm.$^{-1}$.

Attempts to prepare a semicarbazone, an acetyl derivative, or an enol-acetate led to recovery of 3β-dimethylamino-5-hydroxy-6-oxoconanine which did not react with selenium dioxide, *N*-bromosuccinimide, benzaldehyde, potassium periodate, or phosphorus oxychloride. When 3β-dimethylamino-5-hydroxy-6-oxoconanine was refluxed for 117 hr. with 98—100% formic acid it was converted into an *isomer* which separated from acetone in long needles, m. p. 193—195° (Found: C, 73·8; H, 10·5; N, 7·5. $C_{24}H_{40}O_2N_2$ requires C, 74·2; H, 10·4; N, 7·2%). The acetone mother-liquors after evaporation, dissolution in ether, adsorption on alumina, and elution with ether-chloroform (1 : 1) yielded a *substance* which crystallised from acetone–light petroleum in prisms, m. p. 204—205° (decomp.) (Found: C, 76·9; H, 9·9; N, 4·1. $C_{22}H_{33}O_2N$ requires C, 76·9; H, 9·7; N, 4·1%).

Oxidation of Dioxyconessine with Warm Chromic Acid.—Chromium trioxide (5·5 g.) in water (200 ml.) was slowly added to a solution of dioxyconessine (11 g.) in 10% sulphuric acid (100 ml.) on the steam-bath. After 1 hr. the cooled mixture was basified with barium hydroxide, the precipitated chromium hydroxide and barium sulphate were removed on a centrifuge and washed with warm water, the combined washings and aqueous liquors were heated to the b. p., and the volatile bases passed into aqueous picric acid. Dimethylamine picrate was isolated; it had m. p. 157—158° after crystallisation from alcohol. Carbon dioxide passed through the non-volatile aqueous solution precipitated barium carbonate which was removed. The filtrate was evaporated to dryness under reduced pressure. The amino-acid mixture remained as a friable mass (8·8 g.) which crystallised, with difficulty, from acetone containing a small amount of water and gave 5-*oxo*-5 : 6-seco*con*-3-*enin*-6-*oic acid sesquihydrate* (cf. IX; R = H) as colourless prisms, m. p 193—196° (decomp.) (Found: C, 68·7; H, 9·2; N, 4·0. $C_{22}H_{33}O_3N,1\frac{1}{2}H_2O$ requires C, 68·3; H, 9·4; N, 3·6%), $\lambda_{max.}$ 2270 Å (log ε 4·0). The water of crystallisation was retained at 60°/0·01 mm. for 12 hr. The amino-acid mixture (6·5 g.), heated for 6 hr. with saturated ethanolic hydrogen chloride (150 ml.), gave a brown gum (6·3 g.), which was chromatographed in light petroleum on alumina (120 g.). A light petroleum–benzene (1 : 1) eluate (3·3 g.) yielded *ethyl* 5-*oxo*-5 : 6-seco*con*-3-*enin*-6-*oate* (IX; R = Et) as a pale yellow oil, b. p. 195° (bath)/0·03 mm. (Found: C, 74·2; H, 9·9; N, 3·6. $C_{24}H_{37}O_3N$ requires C, 74·4; H, 9·6; N, 5·6%), $\lambda_{max.}$ 2270 Å (log ε 4·0).

Further elution of the alumina with ether yielded a *substance* which separated from light petroleum in colourless needles (120 mg.), m. p. 103—104° (Found: C, 75·3, 75·2; H, 9·8, 10·0; N, 3·0, 3·3. $C_{26}H_{41}O_3N$ requires C, 75·2; H, 9·9; N, 3·4%), which was not identified.

Pyrolysis of 5-*Oxo*-5 : 6-seco*con*-3-*enin*-6-*oic Acid* (IX; R = H).—The amino-acid mixture (6·2 g.) was mixed with dry potassium carbonate (15 g.) and iron filings (6 g.) and heated with a free flame. Water and carbon dioxide were eliminated and a yellow oil distilled. The combined distillates from two such operations were mixed with the ether extract from the

non-volatile material. The non-basic fraction (380 mg.) remained in the ether after washing with dilute hydrochloric acid, and the basic material (4·82 g.) was recovered by basification, isolated with ether, and chromatographed in light petroleum–benzene (1 : 1) on alumina (125 g.). Elution with the same solvent gave B-norcona-3 : 5-diene (X) as an oil (2·20 g.) which with methyl iodide in warm benzene gave the *methiodide*, crystallising from acetone in colourless plates, m. p. 265—267° (Found: C, 60·0; H, 7·9; N, 2·8. $C_{22}H_{34}NI$ requires C, 60·1; H, 7·8; N, 3·2%). The oil (X) had $\lambda_{max.}$ 2400 (log ε 4·1) and 2450 Å (log ε 4·1), but did not react with maleic anhydride. Further elution of the alumina with benzene removed a *ketone* as an oil which slowly crystallised; the crystals (190 mg.) were sublimed at 80°/0·01 mm. and recrystallised from aqueous acetone in colourless needles, m. p. 98—99° (Found: C, 77·9, 77·9; H, 10·2, 10·4; N, 5·4. $C_{17}H_{27}ON$ requires C, 78·1; H, 10·4; N, 5·4%), having infrared bands at, *inter al.*, 3436 and 1738 cm.$^{-1}$, giving a positive Liebermann test and a *semicarbazone* which separated from aqueous acetone in colourless needles, m. p. 162—163° (Found: N, 15·8. $C_{18}H_{30}ON_4,2H_2O$ requires N, 15·8%).

Hydrogenation of B-*Norcona*-3 : 5-*diene* (X).—The diene (196 mg.) in ethanol (10 ml.) was hydrogenated at room temperature in the presence of 5% palladium–charcoal (390 mg.). The uptake of hydrogen was slow and the saturation of one double bond (uptake: 18·9 ml.) occupied 12 hr. The dihydro-compound (180 mg.) was an oil with no characteristic ultraviolet maximum, and readily liberated iodine from iodic acid. The *methiodide*, prepared in benzene, crystallised from acetone–ether in colourless plates, m. p. 257—258° (Found: C, 59·8, 60·0; H, 8·5, 8·3; N, 2·8, 2·9; I, 29·1. $C_{22}H_{36}NI$ requires C, 59·85; H, 8·2; N, 3·2; I, 28·8%).

Pyrolysis of 5-*Oxo*-5 : 6-seco*conanin*-6-*oic acid* (XIII).—The amino-acid mixture (15 g.) [containing (IX; R = H)] in ethanol (100 ml.) was shaken with hydrogen in presence of 10% palladium–charcoal (4 g.) for 15 hr.; hydrogen uptake was then complete. Filtration and evaporation of the solvent gave 5-oxo-5 : 6-*seco*conanin-6-oic acid (XIII) as a light brown friable mass, the alcoholic solution of which showed no characteristic ultraviolet absorption. A mixture of the crude reduction product (6·6 g.) and dry potassium carbonate (3·3 g.) was heated, water and carbon dioxide being evolved. The residue was distilled under reduced pressure, the products from two such operations were combined, and the basic fraction (6·2 g.) was isolated as described for an analogous case above. A light petroleum solution of the basic fraction was chromatographed on alumina (180 g.) and eluted first with the same solvent to give a colourless oil (*A*) (3·37 g.) and then with ether–light petroleum (1 : 1) to yield a pale yellow oil (*B*) (1·65 g.). The oil (*A*) slowly solidified and crystallisation from acetone gave B-*norcon*-5-*enine* (XIV) as stout colourless needles, m. p. 78—79° (Found: C, 84·1; H, 11·4; N, 4·6. $C_{21}H_{33}N$ requires C, 84·2; H, 11·1; N, 4·7%). The acetone mother-liquors gradually deposited a dimorphous *form* as colourless rectangular prisms, m. p. 78—79° (Found: C, 84·1; H, 11·2; N, 5·2%), and when inoculated with this prismatic form the oil (*B*) rapidly solidified, and in subsequent reactions the dimorphous forms were indistinguishable. The base liberated iodine from iodic acid, but showed no characteristic ultraviolet absorption. The *hydrochloride*, prepared with ethereal hydrogen chloride, separated from methanol–acetone in colourless needles, m. p. 268° (decomp.) (Found: C, 74·7; H, 10·0; N, 4·2; Cl, 11·0. $C_{21}H_{34}NCl$ requires C, 75·1; H, 10·2; N, 4·2; Cl, 10·6%). The *picrate*, prepared from aqueous solution, crystallised from aqueous acetone in yellow needles, m. p. 100° (Found: C, 59·7; H, 7·2; N, 10·2. $C_{21}H_{33}N,C_6H_3O_7N_3,H_2O$ requires C, 59·3; H, 7·0; N, 10·1%). The *methiodide*, prepared in benzene, crystallised from acetone–benzene in colourless plates, m. p. 261—262° (Found: C, 60·0; H, 7·9; N, 2·9. $C_{21}H_{33}N,CH_3I$ requires C, 59·5; H, 8·2; N, 3·2%). The *dihydro-derivative* (B-*norconanine*), prepared in acetic acid solution by using Adams platinic oxide, crystallised from acetone in large prisms, m. p. 67—68° (Found: C, 83·6; H, 11·5; N, 4·2. $C_{21}H_{35}N$ requires C, 83·6; H, 11·7; N, 4·6%), which did not liberate iodine from iodic acid.

Action of Dilute Hydrochloric Acid on B-*Norcon*-5-*enine* (XIV).—An ethereal solution of the base (XIV) was treated with 2N-hydrochloric acid, and the crystalline hydrochloride which separated from the aqueous phase was collected. The crystals became gummy overnight in a vacuum-desiccator and, when the gum was warmed on the steam-bath with dilute hydrochloric acid, the solution became cloudy and after 40 min. set to a crystalline mass. These crystals were collected and dried; recrystallisation from methanol–acetone gave the isomeric *hydrochloride* in colourless needles, m. p. 274° (decomp.) (Found: C, 73·1; H, 10·3; N, 4·4; Cl, 9·8. $C_{21}H_{33}N,HCl,\frac{1}{2}H_2O$ requires C, 73·1; H, 10·2; N, 4·1; Cl, 10·3%). The isomeric base [B-*norcon*-8(9)-*enine*] (XV) was obtained as stout needles, m. p. 114·5—115° (Found: C, 84·0;

H, 11·3; N, 5·2. $C_{21}H_{33}N$ requires C, 84·2; H, 11·1; N, 4·7%), unchanged after attempted reduction in acetic acid in presence of Adams platinic oxide.

Action of Periodic Acid on B-*Norcon-5-enine* (XIV).—The base (XIV) (128 mg.) was added to a solution of potassium periodate (1 g.) in N-sulphuric acid (40 ml.). After 20 hr. at room temperature, the solution was cooled to 0° and basified with sodium hydroxide. The product, isolated with ether, was a gum (120 mg.) which gave 4 : 5 : 6-*trihydroxy*-B-*norconanine* (XVII) as colourless prisms (38 mg.), m. p. 234—235° (decomp.) (Found: C, 71·9; H, 10·1; N, 4·5. $C_{21}H_{35}O_3N$ requires C, 72·2; H, 10·1; N, 4·0%), on crystallisation from methanol–acetone. The mother-liquors were evaporated; the residue solidified under light petroleum at 0° and after crystallisation from *cyclo*hexane yielded 5 : 6-trans-*dihydroxy*-B-*norconanine* (XVI) as needles (35 mg.), m. p. 168—169° (Found: C, 75·8; H, 10·6; N, 4·5. $C_{21}H_{35}O_2N$ requires C, 75·6; H, 10·6; N, 4·2%).

Action of Osmium Tetroxide on B-*Norcon-5-enine* (XIV).—A solution of the base (XIV) (1 g.) and osmium tetroxide (1 g.) in ether (80 ml.) was refluxed for 120 hr., and the precipitated osmic ester was collected and washed with ether. Evaporation of the filtrate gave unchanged base (XIV) (333 mg.), m. p. 78—79°. After the precipitated osmic ester had been shaken with mannitol (5 g.) and N-potassium hydroxide (30 ml.) for 12 hr., water (52 ml.) was added and the solution was extracted four times with chloroform. The extract was washed with water, the solvent removed, and the residual dark brown gum (650 mg.) chromatographed in ether on alumina (20 g.). Elution with ether yielded a dark brown gum (450 mg.) which crystallised on trituration with light petroleum, and after two crystallisations from *cyclo*hexane 5 : 6-cis-*dihydroxy*-B-*norconanine* was obtained as needles (265 mg.), m. p. 184—185° (Found: C, 75·4; H, 10·5; N, 4·5. $C_{21}H_{35}O_2N$ requires C, 75·6; H, 10·6; N, 4·2%).

Action of Periodic Acid on 5 : 6-cis-*Dihydroxy*-B-*norconanine* (XVI).—After 40 hr. at room temperature a solution of the *cis*-diol (100 mg.), potassium periodate (100 mg.), and N-sulphuric acid (5 ml.) was cooled to 0°, then basified with dilute sodium hydroxide; 4 : 8-*hydroxymethylene*-5-*oxo*-5 : 8-seco-B-*bisnorconanine* (XIX) (95 mg.), isolated with ether, separated from *cyclo*hexane in needles, m. p. 179—180° (Found: C, 76·4; H, 10·1; N, 4·5. $C_{21}H_{33}O_2N$ requires C, 76·1; H, 10·0; N, 4·2%). The infrared spectrum had, *inter al.*, bands at 1700 and 3345 $cm.^{-1}$. The *semicarbazone*, prepared in methanol, crystallised from acetone in colourless plates, m. p. 220—221° (Found: N, 14·4. $C_{22}H_{36}O_2N_4$ requires N, 14·4%).

Action of Alkali on 4 : 8-*Hydroxymethylene*-5-*oxo*-5 : 8-seco-B-*bisnorconanine* (XIX).—The aldol (XIX) (50 mg.) in methanol was heated for 90 min. in a nitrogen atomosphere with potassium hydroxide (160 mg.) in water (1 ml.). Water (5 ml.) was added and the solution neutralised to pH 7 with 2N-sulphuric acid. The precipitate (29 mg.) was collected and crystallised twice from light petroleum; 5-*hydroxy*-5 : 6-seco-B-*norconanin*-6-*oic* 5 : 6-*lactone* (XX) separated in colourless prisms, m. p. 131—132° (Found: C, 76·0; H, 10·0; N, 3·8. $C_{21}H_{33}O_2N$ requires C, 76·1; H, 10·0; N, 4·2%).

Pyrolysis of 4 : 8-*Hydroxymethylene*-5-*oxo*-5 : 8-seco-B-*bisnorconanine* (XIX).—The aldol (XIX) (328 mg.) was mixed with potassium carbonate (164 mg.) and pyrolysed with a free flame. The product, treated as described previously for an analogous case, gave non-basic (42 mg.) and basic fractions (109 mg.); the former was identified as 2-methyl*cyclo*hexanone by the preparation of the 2 : 4-dinitrophenylhydrazone, m. p. 134—135°. The basic material, which showed no characteristic maximum in the ultraviolet spectrum, was chromatographed in light petroleum on alumina (3 g.). Elution with the same solvent gave an oil (16 mg.), which yielded a picrate, m. p. 226° (decomp.) after crystallisation from acetone; the quantities were insufficient for analysis or further examination.

Oxidation of 4 : 8-*Hydroxymethylene*-5-*oxo*-5 : 8-seco-B-*bisnorconanine* (XIX).—A solution of the aldol (XIX) (100 mg.) and chromium trioxide (31 mg.) in acetic acid (9·5 ml.) and water (0·5 ml.) was kept at room temperature for 50 hr., and excess of oxidising agent was then removed by warm alcohol (5 ml.). Most of the acetic acid was removed *in vacuo*, the solution was basified with dilute sodium hydroxide solution, and 4 : 8-*carbonyl*-5-*oxo*-5 : 8-seco-B-*bisnorconanine* (XXI) isolated with ether; it crystallised from aqueous acetone in colourless needles, m. p. 121—122° (Found: C, 76·0; H, 9·4; N, 4·5. $C_{21}H_{31}O_2N$ requires C, 76·5; H, 9·5; N, 4·3%).

Action of Alkali on 4 : 8-*Carbonyl*-5-*oxo*-5 : 8-seco-B-*bisnorconanine* (XXI).—The diketone (XXI) (100 mg.), barium hydroxide (5 ml. of saturated solution), and water (5 ml.) were heated for 2 hr. on the steam-bath. After removal of unchanged diketone (3 mg.) with ether, the

aqueous liquors were saturated with carbon dioxide, and the barium carbonate was removed. Evaporation of the filtrate gave crude 5-oxo-5 : 6-*seco*-B-norconanin-6-oic acid (XXII; R = H) which was esterified with ethereal diazomethane; the *methyl ester* (XXII; R = Me) separated from light petroleum in stout prisms, m. p. 131—132° (Found: C, 72·9; H, 9·8; N, 3·9. $C_{22}H_{35}O_3N$ requires C, 73·1; H, 9·8; N, 3·9%). The ester methiodide crystallised from acetone in colourless prisms, m. p. 290° (decomp.).

Preparation of Methyl 5-Oxo-5 : 6-seco-B-norconanin-6-oate (XXII; R = Me) *from 5 : 6-cis-Dihydroxy-B-norconanine* (XVI).—A solution of the *cis*-diol (XVI) (100 mg.) in 10% sulphuric acid (1 ml.) was warmed on the steam-bath with chromium trioxide (40 mg.) in water (2 ml.) for 30 min. Isolation of the amino-acid fraction as described for dioxyconessine gave a gum (52 mg.) which, methylated in ether with diazomethane, gave methyl 5-oxo-5 : 6-*seco*-B-norconanin-6-oate (XXII; R = Me), m. p. 131—132°, identical with that obtained from the diketone (XXI).

Pyrolysis of Methyl 5-Oxo-5 : 6-seco-B-norconanin-6-oate (XXII; R = Me).—The ester (50 mg.) was heated at 335—340° in an evacuated sealed tube, and the product chromatographed in light petroleum on alumina (1 g.). Elution with light petroleum–ether (1 : 1) gave 5-hydroxy-5 : 6-*seco*-B-norcon-4-enin-6-oic 5 : 6-lactone (XXIII) as a pale yellow oil (25 mg.) which did not crystallise on inoculation with starting material. The *methiodide* separated from methanol–acetone in colourless prisms, m. p. 299—300° (decomp.) (Found: C, 55·05; H, 7·4; N, 3·1. $C_{21}H_{31}O_2N,CH_3I,\frac{1}{2}H_2O$ requires C, 55·0; H, 7·3; N, 2·9%).

Pyrolysis of 5-Oxo-5 : 6-seco-B-norconanin-6-oic Acid (XXII; R = H).—The amino-acid (200 mg.) was mixed with dry potassium carbonate (100 mg.) and heated with a free flame until distillation ceased. The distillates from four such operations were combined and separated into non-basic (160 mg.) and basic (380 mg.) fractions. 2-Methyl*cyclo*hexanone, isolated as the 2 : 4-dinitrophenylhydrazone, m. p. 133—134°, was obtained from the non-basic fraction. The basic material was treated with light petroleum, filtered from insoluble material (120 mg.), and chromatographed on alumina (9 g.). Elution with light petroleum gave a colourless odourless oil (*A*; 50 mg.) and light petroleum–ether (1 : 1) removed a pale yellow oil (*B*; 132 mg.) with a powerful odour.

Fraction *A* gave a picrate which, after three crystallisations from ethanol, gave the *picrate of des-AB-con-8-enine* (XXIV; R = Me) as straw-coloured needles, m. p. 178—179° (decomp.) (Found: C, 54·0; H, 5·7; N, 13·4. $C_{19}H_{24}O_7N_4$ requires C, 54·3; H, 5·75; N, 13·3%). The free base, isolated from the pure picrate (18 mg.) on treatment with lithium hydroxide, was reduced with Adams platinum oxide and hydrogen in acetic acid. The picrate of the des-AB-conanine was obtained as yellow needles, m. p. 153—154°, from aqueous acetone but there was insufficient for analysis.

Fraction *B* was converted into the picrate which separated from a little acetone in dark yellow needles. Two crystallisations from acetone–carbon tetrachloride gave *de*-N-*methyldes-AB-con-8-enine picrate* (cf. XXIV; R = H) as yellow needles, m. p. 236—238° (decomp.) (evacuated tube; bath preheated to 230°) (Found: C, 53·3; H, 5·3; N, 14·0. $C_{18}H_{22}O_7N_4$ requires C, 53·2; H, 5·5; N, 13·8%). The picrate (9 mg.) was decomposed with lithium hydroxide, and de-*N*-methyldes-AB-con-8-enine (XXIV; R = H) extracted into ether. It had a very powerful odour and gave a positive Liebermann nitroso-test.

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