A Simple Route to Spiro[indene-2,1'-isoquinoline]s, a Spiro[indene-2,1'-β-carboline], and Hexadehydroyohimbane

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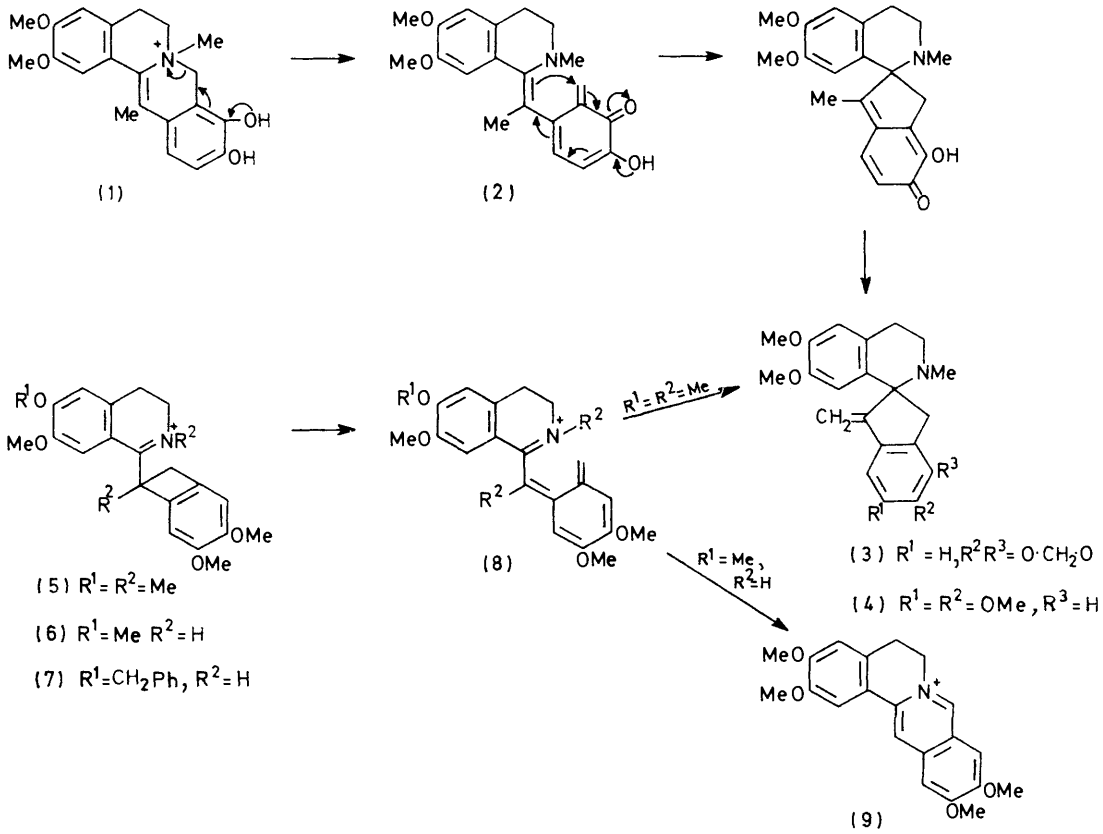
1',2,2',3,3',4'-Hexahydro-5,6,6',7'-tetramethoxyspiro[indene-2,1'-isoquinolin]-1-one (13) and its 6'-benzyloxy-analogue (14) were synthesised from 3,4-dihydro-1-(1,2-dihydro-4,5-dimethoxybenzocyclobuten-1-yl)isoquinolines [(6) and (7)]. Autoxidation of the 1-(1,2-dihydrobenzocyclobuten-1-yl)-β-carboline (26) gave the spiro[indene-2,1'-β-carbolin]-1-one, which was converted photochemically into the hexadehydroyohimbane (29).

SHAMMA [1] has suggested that the spirobenzylisoquinoline alkaloids, such as ochotensimine (3), could be biosynthesised from the berbinium-type compounds (1) through the *o*-quinonoid intermediate (2), and has succeeded in the chemical conversion of a diphenolic ever the 3,4-dihydro-1-(1,2-dihydrobenzocyclobutenyl)-isoquinolinium chloride was transformed into the berbinium system (9) on heating at 150—160°.[4,5] We now report the transformation of the free base corresponding to structure (6) into a spirobenzylisoquinoline,



SCHEME 1

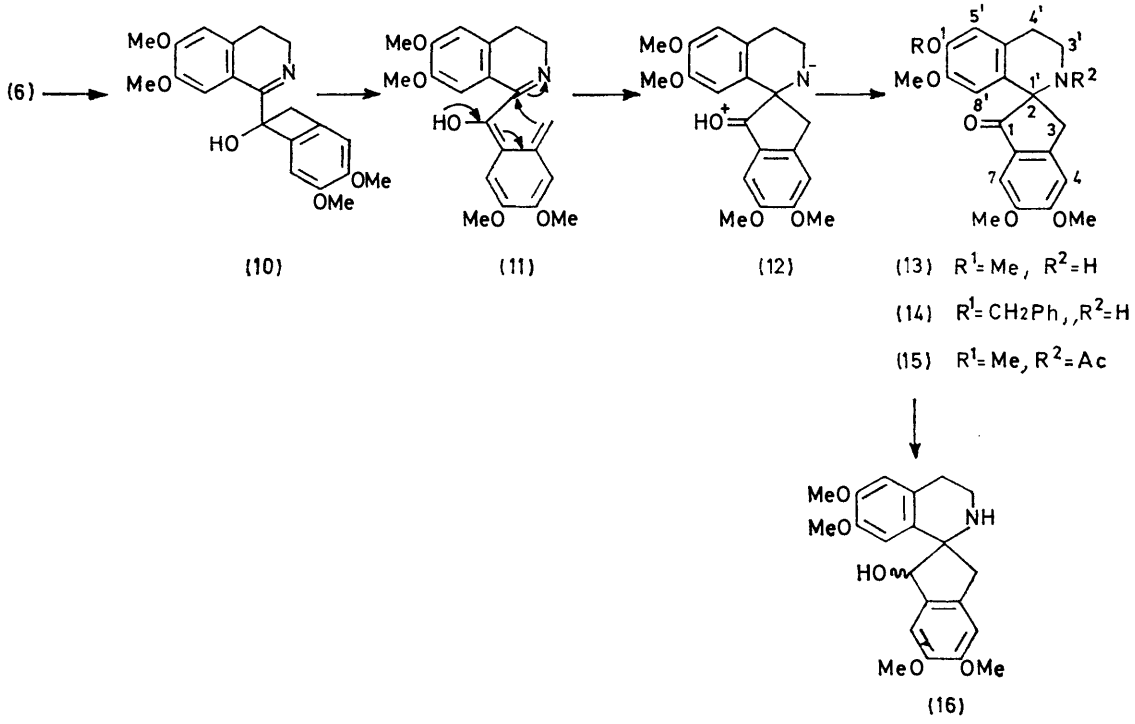
N-metho-salt into an ochotensine-type compound.[1,2] We have reported the synthesis of the spirobenzylisoquinoline (4) from the *o*-quinodimethane (8), an electronic equivalent of the *o*-quinonoid intermediate (2), generated thermally from the 3,4-dihydro-1-(1,2-dihydrobenzocyclobuten-1-yl)-2-methylisoquinolinium salt (5).[3] and also the photochemical conversion of an analogous spiro-product into a quinolizine system.

Although the hydrochloride of the 1-benzocyclobutenylisoquinoline (6) [4] is stable at room temperature in organic solvents, when the free base [m.p. 135—136° (decomp.); $\nu_{max.}$ ($CHCl_3$) 1620sh cm^{-1} (C=N); *m/e* 353

[1] M. Shamma and C. D. Jones, *J. Amer. Chem. Soc.*, 1969, **71**, 4009; 1970, **92**, 4943.
[2] M. Shamma and J. F. Nugent, *Tetrahedron*, 1973, **29**, 1265; *Tetrahedron Letters*, 1970, 2625; *Chem. Comm.*, 1971, 1642.
[3] T. Kametani, T. Takahashi, and K. Ogasawara, *Tetrahedron Letters*, 1972, 4847; *J.C.S. Perkin I*, 1973, 1464.
[4] T. Kametani, K. Ogasawara, and T. Takahashi, *J.C.S. Chem. Comm.*, 1972, 675; *Tetrahedron*, 1973, **29**, 73; T. Kametani, Y. Hirai, F. Satoh, K. Ogasawara, and K. Fukumoto, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 907.
[5] M. Shamma, 'The Isoquinoline Alkaloids,' Academic Press, New York, 1972, pp. 381—398.

(M^+); δ ($CDCl_3$) 3·82 (6H, s, 2 × OMe), 3·85 (3H, s, OMe), 3·90 (3H, s, 2 × OMe), 4·72br (1H, >C*H*·CH_2), 6·70 (3H, s, 3 × ArH), and 7·07 (1H, s, ArH)] was kept in chloroform at room temperature for 24 h it was converted into a new base, m.p. 204—205°, in 63·5% yield. The product was assigned structure (13) on the basis of spectroscopic data. The mass spectrum [*m/e* 369 (M^+)] showed that one more oxygen atom had been introduced, and the i.r. [$\nu_{max.}$ (KBr) 3305 (NH) and 1690 cm^{-1} (C=O)] and u.v. spectra [$\lambda_{max.}$ (MeOH) 321 and 275 nm] revealed the presence of *N*-unsubstituted 1,2,3,4-tetrahydroisoquinoline and aroyl systems. The presence of the NH group was proved by the formation of the amide (15), [$\nu_{max.}$ (KBr) 1700 and 1640 cm^{-1}] by treatment with acetic anhydride–pyridine. The n.m.r. spectrum (solvent $CDCl_3$) showed four methoxy-resonances at δ 3·59, 3·82, 3·91, and 3·97, a benzyl methylene signal at 3·37 as a singlet, singlet signals for four aromatic protons (6·11, 6·58, 6·89, and 7·24), and two CH_2 signals, thus indicating that the new oxygen atom was present in the carbonyl group. Reduction of this product with lithium aluminium hydride gave the carbinol (16), δ ($CDCl_3$) 4·95 (1H, s, C*H*·OH). The spirobenzylisoquinoline structure (13) was further supported by the presence of the characteristic high-field methoxy- (δ 3·59) and aromatic proton (δ 6·11) resonances in its n.m.r. spectrum,[5] confirmed by spectral comparison with an authentic sample prepared by Irie.[6]

A possible mechanism for the formation of the spirobenzylisoquinoline (13) is shown in Scheme 2. Autoxidation * of the free base (6) gives the unstable intermediate (10), ring-opening of which according to the Woodward–Hoffmann rules,[8] followed by an electrocyclic process involving the (*E*)-*o*-quinodimethane (11), affords the spirobenzylisoquinoline (13) through the intermediate (12).



SCHEME 2

Similarly, the free base corresponding to the 6-benzyloxy-analogue (7) of (6) was transformed into the spirobenzylisoquinoline (14) [ν_{max} (KBr) 3325 and 1680 cm^{-1}; δ ($CDCl_3$) 3·41 (ArCH_2), 3·59 (7′-OMe), and 6·15 (8′-H)].

This type of reaction was then applied to the synthesis of the spiro[indene-2,1′-β-carbolin]-1-one (27), which was converted into the hexadehydroyohimbane (29) by photolysis and then reduction. The starting 1-benzocyclobutenyl-3,4-dihydro-β-carboline (26) was synthesised by established methods [4,9] as follows. Condensation of 2,3,4-trimethoxybenzaldehyde (17) [10] with cyanoacetic acid in the presence of pyridine and ammonium acetate in boiling benzene gave α-cyano-2,3,4-trimethoxycinnamic acid (18), which was reduced with sodium borohydride in sodium hydrogen carbonate

* It is well known [7] that the benzylic methylene group in some 1-benzyl-3,4-dihydroisoquinolines is susceptible to autoxidation.

[6] H. Irie, K. Akagi, S. Tani, K. Yabushi, and H. Yamane, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 855.

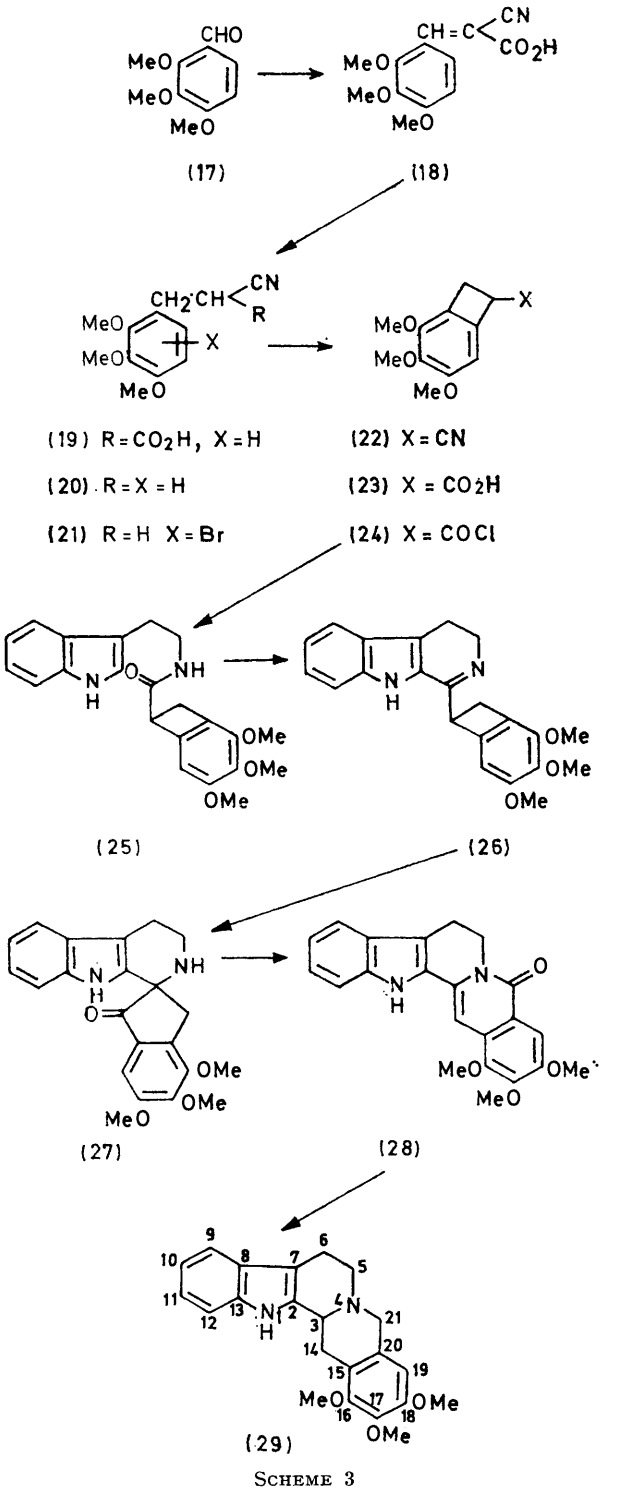
[7] T. Kametani, S. Kano, Y. Watanabe, and T. Kikuchi, *J. Pharm. Soc. Japan*, 1967, **87**, 406.

[8] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1969.

[9] T. Kametani, M. Kajiwara, and K. Fukumoto, *Chem. and Ind.*, 1973, 1165.

[10] P. E. Papadakis and W. Boand, *J. Org. Chem.*, 1961, **26**, 2075.

solution to afford the dihydrocinnamic acid (19). This was decarboxylated in *NN*-dimethylacetamide at 150°



SCHEME 3

and the resulting phenylpropiononitrile (20) was treated with bromine in the presence of sodium acetate in acetic acid to give the bromophenylpropiononitrile (21). The position of the bromine atom was not determined. Treatment of the brominated nitrile (21) with sodium amide in liquid ammonia furnished the cyanobenzocyclobutene (22), which on hydrolysis with potassium hydroxide gave the corresponding carboxylic acid (23). Schotten–Baumann reaction of the derived acid chloride (24) with tryptamine in the presence of sodium hydroxide in chloroform afforded the amide (25), which was subjected to Bischler–Napieralski reaction with phosphoryl chloride in boiling benzene to yield the benzocyclobutenyl-β-carboline (26), characterised as the hydrochloride.

The free base (26) was converted into the spirobenzyl-β-carboline (27) in 84% yield when kept at room temperature for 3 days in chloroform. Photolysis [6, *] of this product with a Hanovia 450 W mercury lamp in dry tetrahydrofuran in a current of nitrogen at room temperature for 2·5 h gave the decadehydroyohimban-21-one (28) in 26% yield, which was identified by spectroscopic methods. The i.r. spectrum showed an amide carbonyl band at 1640 and olefinic absorption at 1615 cm^{-1}, and the u.v. spectrum [$\lambda_{max.}$ (MeOH) 371, 347, 333, 272sh, 255, and 229 nm] revealed the presence of the decadehydroyohimban-21-one system.[12] The n.m.r. spectrum showed the 14- and 19-H signals at δ 7·01 and 7·68, each as a singlet. Reduction of (28) with lithium aluminium hydride in boiling tetrahydrofuran, followed by treatment of the hydrochloride of the crude product with sodium borohydride, gave the hexadehydroyohimbane (29), identified from spectral data.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto micro-apparatus (MP-S2). I.r. spectra were measured with a Hitachi 215 grating spectrophotometer, n.m.r. spectra with a Hitachi H-60 spectrometer with tetramethylsilane as internal standard, mass spectra with a Hitachi RMU-7 spectrometer, and u.v. spectra with a Hitachi 124 spectrometer.

1′,2,2′,3,3′,4′-*Hexahydro*-5,6,6′,7′-*tetramethoxyspiro*-[*indene*-2,1′-*isoquinolin*]-1-*one* (13).—A solution of 3,4-dihydro-1-(1,2-dihydro-4,5-dimethoxybenzocyclobuten-1-yl)-6,7-dimethoxyisoquinoline [4] [prepared from the hydrochloride (6) (100 mg) and 10% ammonia in chloroform] in chloroform (25 ml) was set aside at room temperature for 24 h and the solvent was then distilled off *in vacuo*. The residue was dissolved in benzene and the solution was washed with aqueous 5% sodium hydrogen carbonate and extracted with 10% hydrochloric acid. The extract was basified with 10% sodium hydroxide and the material separated was extracted with chloroform. The chloroform extract was washed with water, dried (Na_2SO_4), and evaporated *in vacuo* to give the spirobenzylisoquinoline (13) (60 mg, 63·5%) as yellow needles, m.p. 204—205° (lit.,[6] m.p. 203—205°) (from ethanol), $\nu_{max.}$ (KBr) 3305, 1700, and 1690 cm^{-1}, δ ($CDCl_3$) 3·37 (2H, s, $ArCH_2C$), 3·59 (3H, s, 7′-OMe), 3·82 (3H, s, OMe), 3·91 (3H, s, OMe), 3·97 (3H, s, OMe), 6·11 (1H, s, 8′-H), 6·58 (1H, s, ArH), 6·89 (1H, s, ArH), and 7·24 (1H, s, 7-H), *m/e* 369 (M^+), identical (i.r. and n.m.r. spectra) with an authentic sample.[6]

* The 3,4,14,15,16,17,18,19,20,21-decadehydroyohimban-21-one system has also been obtained from a spirobenzyl-β-carboline by Irie, using the same reaction.[11]

[11] H. Irie, personal communication.

[12] L. Merlini, R. Mondelli, and G. Nasini, *Tetrahedron*, 1967, **23**, 3129.

6′-*Benzyloxy*-1′,2,2′,3,3′,4′-*tetrahydro*-5,6,7′-*trimethoxyspiro*[*indene*-2,1′-*isoquinolin*]-1-*one* (14).—6-Benzyloxy-3,4-dihydro-1-(1,2-dihydro-4,5-dimethoxybenzocyclobuten-1-yl)-7-methoxyisoquinoline [4] [prepared from the corresponding hydrochloride (7) (100 mg)] in chloroform (25 ml) was treated as above to give a crude product. Silica gel (1 g) chromatography (chloroform as eluant) gave the *spirobenzylisoquinoline* (14) (45 mg, 57·4%) as yellow needles, m.p. 158—160° (from ethanol) (Found: C, 71·25; H, 5·95; N, 3·5. $C_{27}H_{27}NO_5,0{\cdot}5H_2O$ requires C, 71·35; H, 6·2; N, 3·1%), $\nu_{max.}$ (KBr) 3325, 1700, and 1680 cm^{-1}; δ ($CDCl_3$) 3·41 (2H, s, ArCH_2C), 3·59 (3H, s, 8′-OMe), 3·90 (3H, s, OMe), 3·98 (3H, s, OMe), 5·07 (2H, s, ArCH_2O), 6·15 (1H, s, 8′-H), 6·61 (1H, s, ArH), 6·90 (1H, s, ArH), 7·26 (1H, s, ArH), and 7·35br (5H, C_6H_5·CH_2O).

1′,2,2′,3,3′,4′-*Hexahydro*-5,6,6′,7′-*tetramethoxyspiro*-[*indene*-2,1′-*isoquinolin*]-1-*ol* (16).—To a suspension of lithium aluminium hydride (100 mg) in anhydrous tetrahydrofuran (30 ml) a solution of the spirobenzylisoquinolinone (13) (500 mg) in tetrahydrofuran (20 ml) was added dropwise with stirring at 0°. The mixture was stirred for 1 h at room temperature, then decomposed with wet ether, and the organic layer was evaporated to give the *carbinol* (16) (470 mg) as needles, m.p. 176—178° (from ethanol) (Found: C, 67·85; H, 6·8; N, 3·7. $C_{21}H_{25}NO_5$ requires C, 67·9; H, 6·8; N, 3·75%), $\nu_{max.}$ (KBr) 3330—3580 and 3280 cm^{-1}; δ ($CDCl_3$) 3·55 (3H, s, 7′-OMe), 3·80 (3H, s, OMe), 3·85 (6H, s, 2 × OMe), 4·95 (1H, s, ArC*H*OH), 6·52 (1H, s, ArH), 6·56 (1H, s, ArH), 6·72 (1H, s, ArH), and 6·90 (1H, s, ArH).

2′-*Acetyl*-1′,2,2′,3,3′,4′-*hexahydro*-5,6,6′,7′-*tetramethoxyspiro*[*indene*-2,1′-*isoquinolin*]-1-*one* (15).—A mixture of the spirobenzylisoquinolinone (13) (100 mg), acetic anhydride (2 ml), and pyridine (1 drop) was kept at room temperature overnight and then poured into water and basified with 10% sodium hydroxide. The material separated was extracted with chloroform and the extract was washed with water, dried (Na_2SO_4), and evaporated *in vacuo* to give the *amide* (15) (80 mg) as needles, m.p. 185—187° (from benzene) (Found: C, 67·35; H, 6·15; N, 3·35. $C_{23}H_{25}NO_6$ requires C, 67·15; H, 6·1; N, 3·4%), $\nu_{max.}$ (KBr) 1700 and 1640 cm^{-1}, δ ($CDCl_3$–CF_3·CO_2H) 2·32 (3H, s, COMe), 3·54 (3H, s, 7′-OMe), 3·90 (3H, s, OMe), 3·98 (3H, s, OMe), 4·05 (3H, s, OMe), 6·26 (1H, s, 8′-H), 6·78 (1H, s, ArH), 7·02 (1H, s, ArH), and 7·38 (1H, s, ArH).

α-*Cyano*-2,3,4-*trimethoxycinnamic Acid* (18).—A mixture of 2,3,4-trimethoxybenzaldehyde (17) [10] (50 g), cyanoacetic acid (26 g), ammonium acetate (1·5 g), pyridine (50 ml), and dry benzene (100 ml) was refluxed (Dean–Stark apparatus) for 1·5 h, then cooled. The yellow crystals which separated were collected and washed with benzene to give the *cinnamic acid* (18) (60 g) as yellow needles (from benzene), m.p. 229—231° (Found: C, 59·65; H, 5·05; N, 5·4. $C_{13}H_{13}NO_5$ requires C, 59·3; H, 5·0; N, 5·2%), $\nu_{max.}$ (KBr) 2220 and 1665 cm^{-1}; δ (CF_3·CO_2H) 4·04 (6H, s, 2 × OMe), 4·10 (3H, s, OMe), 7·10 (1H, d, *J* 9·0 Hz, 6-H), 8·31 (1H, d, *J* 9·0 Hz, 5-H), and 8·89 (1H, s, ArC*H*=C).

α-*Cyano*-β-(2,3,4-*trimethoxyphenyl*)*propionic Acid* (19).—To a solution of the cinnamic acid (18) (63 g) in saturated aqueous sodium hydrogen carbonate (500 ml), sodium borohydride (21 g) was added in portions with stirring at room temperature, and stirring was continued for 1 h at room temperature. The solvent was evaporated off *in vacuo* and the residue was acidified with 10% hydrochloric acid and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to give the *phenylpropionic acid* (19) (58 g) as prisms, m.p. 113—113·5° (from benzene) (Found: C, 58·7; H, 5·65; N, 5·35. $C_{13}H_{15}NO_5$ requires C, 58·55; H, 5·7; N, 5·3%), $\nu_{max.}$ ($CHCl_3$) 2250 and 1715 cm^{-1}; δ ($CDCl_3$) 2·96—3·49 (3H, CH_2·C*H*), 3·83 (6H, s, 2 × OMe), 3·92 (3H, s, OMe), 6·57 (1H, d, *J* 8·0 Hz, 5-H), and 6·70 (1H, d, *J* 8·0 Hz, 6-H).

β-(2,3,4-*Trimethoxyphenyl*)*propiononitrile* (20).—A solution of the phenylpropionic acid (19) (220 g) in *NN*-dimethylacetamide (500 ml) was heated at 150° for 3·5 h, then poured into water. The separated oil was extracted with ether, and the extract was washed with water, dried (Na_2SO_4), and evaporated to give the *phenylpropiononitrile* (20) (166 g) as prisms, m.p. 70·5—71·5° (from ethanol) (Found: C, 65·5; H, 6·9; N, 6·45. $C_{12}H_{15}NO_3$ requires C, 65·15; H, 6·85; N, 6·35%), $\nu_{max.}$ ($CHCl_3$) 2240 cm^{-1}; δ ($CDCl_3$) 2·39—3·02 (4H, CH_2·CH_2), 3·81 (6H, s, 2 × OMe), 3·87 (3H, s, OMe), 6·54 (1H, d, *J* 9·0 Hz, 5-H), and 6·83 (1H, d, *J* 9·0 Hz, 6-H).

β-[5(*or* 6)-*Bromo*-2,3,4-*trimethoxyphenyl*]*propiononitrile* (21).—To a solution of the phenylpropiononitrile (20) (33·5 g) and sodium acetate (2·45 g) in acetic acid (250 ml), bromine (24·2 g) was added dropwise with stirring at room temperature during 40 min, and the mixture was stirred for 1 h and then poured into water. The separated oil was extracted with ether, and the extract was washed with saturated aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and distilled to give the bromophenylpropiononitrile (21) (42·2 g) as an oil, b.p. 157—174° at 2 mmHg, $\nu_{max.}$ ($CHCl_3$) 2250 cm^{-1}; δ (CCl_4) 2·31—2·98 (4H, m, CH_2·CH_2), 3·81 (3H, s, OMe), 3·83 (3H, s, OMe), 3·86 (3H, s, OMe), and 7·02 (1H, s, ArH).

1,2-*Dihydro*-3,4,5-*trimethoxybenzocyclobutene*-1-*carbonitrile* (22).—To a solution of sodium amide [prepared from sodium (12 g), liquid ammonia (2 l), and a trace of iron(III) chloride] in liquid ammonia, the bromide (21) (40 g) was added in portions and the mixture was stirred for 3 h. After evaporation of ammonia, ammonium chloride (44 g) was added and the mixture was treated with water. The separated material was extracted with ether, and the extract was washed with water, dried (Na_2SO_4), and evaporated to give the *benzocyclobutene* (22) (26·1 g) as prisms, m.p. 65—66° (from ethanol) (Found: C, 65·6; H, 6·0; N, 6·3. $C_{12}H_{13}NO_3$ requires C, 65·75; H, 6·0; N, 6·4%), $\nu_{max.}$ ($CHCl_3$) 2240 cm^{-1}; δ ($CDCl_3$) 3·77 (3H, s, OMe), 3·80 (3H, s, OMe), 3·90 (3H, s, OMe), 4·14 (1H, t, *J* 4·5 Hz, C*H*·CH_2), and 6·48 (1H, s, ArH).

1,2-*Dihydro*-3,4,5-*trimethoxybenzocyclobutene*-1-*carboxylic Acid* (23).—A solution of the nitrile (22) (5 g) in saturated ethanolic potassium hydroxide (15 ml) was set aside at room temperature for 20 h and then diluted with water (5 ml). The mixture was refluxed for 3 h and poured into water (300 ml), and the resulting solution was then washed with ether. The aqueous layer was acidified with 10% hydrochloric acid and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to afford the *carboxylic acid* (23) (4·9 g) as prisms, m.p. 144—146° (from benzene) (Found: C, 60·6; H, 5·95. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%), $\nu_{max.}$ ($CHCl_3$) 1700 cm^{-1}; δ ($CDCl_3$) 3·59 (2H, d, *J* 4·5 Hz, CH·CH_2), 3·75 (3H, s, OMe), 3·80 (3H, s, OMe), 3·91 (3H, s, OMe), 4·20 (1H, t, *J* 4·5 Hz, C*H*·CH_2), and 6·44 (1H, s, ArH).

1,2-*Dihydro*-N-(*indol*-3-*ylethyl*)-3,4,5-*trimethoxybenzocyclobutene*-1-*carboxamide* (25).—A mixture of the acid (23) (4·6 g), thionyl chloride (4·6 g), and dry benzene (80 ml) was

refluxed for 0·5 h, and then the excess of reagent and solvent was distilled off *in vacuo* to leave the acid chloride (24) as a viscous syrup.

The crude acid chloride in dry chloroform (50 ml) was added dropwise to a mixture of tryptamine (3·1 g) in chloroform (100 ml) and sodium hydroxide (1 g) in water (50 ml) with stirring at 0° during 0·5 h, and the mixture was then stirred for 0·5 h at room temperature. The organic layer was separated and washed with 5% potassium hydroxide, 10% hydrochloric acid, and water, dried (Na_2SO_4), and evaporated to give the *amide* (25) (7·5 g) as needles, m.p. 83° (from benzene) (Found: C, 69·4; H, 6·4; N, 7·0. $C_{22}H_{24}N_2O_4$ requires C, 69·45; H, 6·35; N, 7·35%), $\nu_{max.}$ (KBr) 2460 and 1640 cm^{-1}; δ ($CDCl_3$) 3·63 (3H, s, OMe), 3·76 (3H, s, OMe), 3·88 (3H, s, OMe), 6·06 (1H, s, ArH), 6·85—7·69 (5H, ArH), and 8·20br (1H, indole NH).

3,4-*Dihydro*-1-(1,2-*dihydro*-3,4,5-*trimethoxybenzocyclobuten*-1-*yl*)-β-*carboline* (26).—A mixture of the amide (25) (5·7 g), phosphoryl chloride (10 g), and dry benzene (200 ml) was refluxed for 3 h, and then the excess of reagent and solvent was distilled off to give the 3,4-*dihydro*-β-*carboline* (26) *hydrochloride* (5 g) as yellow prisms, m.p. 218—220° (decomp.) (from ethanol) (Found: C, 66·4; H, 6·0. $C_{22}H_{23}ClN_2O_3$ requires C, 66·25; H, 5·8%), $\nu_{max.}$ (KBr) 1615 cm^{-1}; $\lambda_{max.}$ (MeOH) 285 and 355 nm; δ ($CF_3{\cdot}CO_2H$) 3·98 (3H, s, OMe), 4·04 (3H, s, OMe), 4·07 (3H, s, OMe), 5·18—5·40 (1H, m, C*H*·CH_2), 6·80 (1H, s, ArH), and 7·20—7·88 (4H, ArH).

1′,2,2′,3,3′,4′-*Hexahydro*-4,5,6-*trimethoxyspiro*[*indene*-2,1′-β-*carbolin*]-1-*one* (27).—A solution of the 3,4-dihydro-β-carboline [prepared from the corresponding hydrochloride (3 g) in the usual way] in chloroform (200 ml) was kept at room temperature for 3 days, then evaporated *in vacuo* to leave the *spiroindene*-β-*carboline* (27) (2·4 g, 84%) as needles, m.p. 227° (from methanol) (Found: C, 69·7; H, 5·95; N, 6·9. $C_{22}H_{22}N_2O_4$ requires C, 69·8; H, 5·85; N, 7·4%), $\nu_{max.}$ ($CHCl_3$) 3450, 3350, and 1697 cm^{-1}; δ [$CDCl_3$–$(CD_3)_2SO$] 3·43 (2H, s, ArCH_2C), 3·87 (3H, s, OMe), 3·91 (6H, s, 2 × OMe), 4·32 br (1H, $CH_2{\cdot}CH$), 6·87—7·56 (5H, ArH), and 10·48 (1H, s, indole N*H*).

3,4,14,15,16,17,18,19,20,21-*Decadehydro*-16,17,18-*trimethoxy-yohimban*-21-*one* (28).—A solution of the spirobenzyl-β-carboline (27) (500 mg) in dry tetrahydrofuran (500 ml) was irradiated with a Hanovia 450 W mercury lamp in a current of nitrogen at room temperature for 2·5 h, and the solvent was then removed by distillation *in vacuo* to give the *yohimbanone* (28) (130 mg, 26%) as yellow prisms, m.p. 246—247° (from chloroform–ether) (Found: C, 69·7; H, 5·75; N, 7·0. $C_{22}H_{20}N_2O_4$ requires C, 70·2; H, 5·35; N, 7·45%), $\nu_{max.}$ ($CHCl_3$) 1640 and 1615 cm^{-1}; $\lambda_{max.}$ (MeOH) 371, 347, 333, 272sh, 255, and 229 nm; δ ($CDCl_3$) 3·10 (2H, t, *J* 6·5 Hz, ArC$H_2{\cdot}CH_2$), 3·86 (3H, s, OMe), 3·95 (6H, s, 2 × OMe), 4·55 (2H, t, *J* 6·5 Hz, $ArCH_2{\cdot}CH_2$), 7·01 (1H, s, 14-H), 7·68 (1H, s, 19-H), and 9·10 (1H, s, NH).

15,16,17,18,19,20-*Hexadehydro*-16,17,18-*trimethoxy-yohimbane* (29).—To a suspension of lithium aluminium hydride (30 mg) in anhydrous tetrahydrofuran (30 ml), the yohimbanone (28) (80 mg) was added in portions, and the mixture was refluxed with stirring for 1 h. After decomposition of the excess of reagent with water, an excess of saturated ethereal hydrogen chloride was added to the organic layer and the solvent was then distilled off *in vacuo*. The residue was dissolved in methanol (30 ml) and to the resulting solution sodium borohydride (50 mg) was added in small portions with stirring at 0°. The mixture was stirred at room temperature overnight, and the methanol was distilled off. The residue was extracted with chloroform and the extract was washed with water, dried (Na_2SO_4), and evaporated to give the *hexadehydro-yohimbane* (29) (40 mg) as needles, m.p. 212—214° (from benzene) (Found: C, 72·4; H, 6·7; N, 7·6. $C_{22}H_{24}N_2O_3$ requires C, 72·5; H, 6·65; N, 7·7%), $\nu_{max.}$ ($CHCl_3$) 3475 and 2850—2750 cm^{-1}; $\lambda_{max.}$ (MeOH) 290, 282, and 276 nm; δ ($CDCl_3$) 3·79 (3H, s, OMe), 3·83 (6H, s, 2 × OMe), 4·17 (1H, d, *J* 15 Hz, 21-H), 6·39 (1H, s, 19-H), 6·77—7·60 (4H, ArH), and 8·12br (1H, NH).

We thank Mrs. H. Hori, Mrs. A. Sato, Mrs. C. Koyanagi, Miss A. Ujie, Miss R. Kato, Miss C. Sato, Miss R. Suenaga, and Mr. T. Ohuchi, Pharmaceutical Institute, Tohoku University, for microanalyses and spectral measurements, and Dr. K. Okui, Research Laboratories, Chugai, Pharmaceutical Co. Ltd., for microanalyses. We also thank Dr. H. Irie, Kyoto University, for providing the i.r. and n.m.r. data of the spirobenzylisoquinoline.

[4/844 *Received*, 26*th April*, 1974]