Stereoselective Synthesis of Lycoranes (2,3,3a,4,5,7-Tetrahydro-1*H*-pyrrolo[3,2,1-*de*]phenanthridines) derived from Alkaloids Lycorine and Caranine

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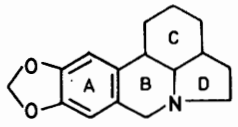
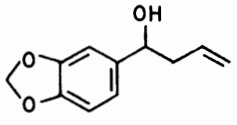
Three stereoisomeric lycoranes (2,3,3a,4,5,7-tetrahydro-1*H*-pyrrolo[3,2,1-*de*]phenanthridines), α-, β-, and δ-lycorane, derived from the Amaryllidaceae alkaloids lycorine and caranine were stereoselectively synthesised from two stereoisomeric 3-(3,4-methylenedioxyphenyl)-1,2,3,6-tetrahydrophthalic anhydrides obtained by Diels–Alder reaction of 1-(3,4-methylenedioxyphenyl)but-3-en-1-ol and fumaric acid.

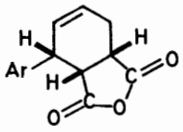
THERE have been several reports [1] concerning the synthesis of lycoranes (I)—(IV),[2] which have been derived from the alkaloids lycorine and caranine. We have



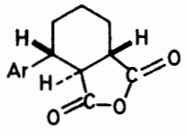
(I) BC *trans*, CD *cis*
(II) BC *trans*, CD *trans*
(III) BC *cis*, CD *cis*
(IV) BC *cis*, CD *trans*



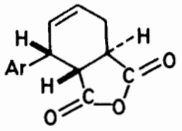
(V)



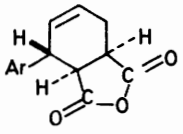
(VI)



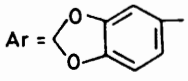
(VII)

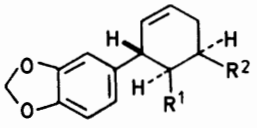


(VIII)



(IX)





(X) $R^1 = CO_2H$; $R^2 = CO_2Me$
(XI) $R^1 = CO_2Me$; $R^2 = CO_2H$
(XII) $R^1 = CON_3$; $R^2 = CO_2Me$
(XIII) $R^1 = N{=}C{=}O$; $R^2 = CO_2Me$

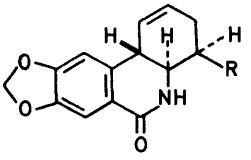
previously reported a synthesis of γ- and δ-lycorane (III) and (IV) starting from the *cis,cis*-phthalic anhydride (VI) which was synthesised by Diels–Alder reaction of the alcohol (V) and maleic anhydride.[3] We report here the synthesis of α-, β-, and δ-lycorane (I), (II), and (IV) using two stereoisomeric anhydrides (VII) and (VIII), both of which were obtained from the Diels–Alder reaction of the alcohol (V) with fumaric acid in acetic anhydride in place of maleic anhydride used for preparation of the anhydride (VI).

Treatment of the alcohol (V) with fumaric acid in acetic anhydride under reflux for 4 h gave three stereoisomeric anhydrides. Careful recrystallisation of the product from benzene provided the *trans,trans*- (VII) and the *cis,trans*-anhydride (VIII) in equal amounts. Column chromatographic separation of the residual mixture from the above recrystallisation on silica gel in chloroform gave a small amount of the *trans,cis*-anhydride (IX) and additional crops of the anhydrides (VII) and (VIII). Formation of the *trans,cis*-anhydride (IX) was explained as being the result of epimerisation of the initially formed cycloaddition products (VII) and (VIII). Haworth and Slinger reported the same type of epimerisation to *trans,cis*-1-phenyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride from the corresponding *trans,trans*-anhydride.[4] Each of the anhydrides (VII) and (VIII) was stereoselectively converted to the same *trans,cis*-anhydride (IX) in good yield by heating in acetic anhydride.

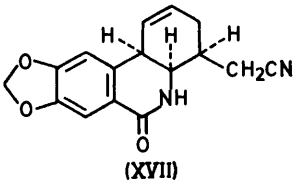
Based on the above findings, in order to secure an ample supply of the *trans,cis*-anhydride (IX) which is a key intermediate for completing the synthesis of Amaryllidaceae alkaloids such as lycorine and clivonine,[5] it was convenient not to isolate each of the anhydrides. Thus, the cycloaddition product was treated with aqueous sodium hydroxide to convert all the anhydrides to the corresponding diacids and a resinous material. The latter was not soluble in aqueous alkali and interfered with the isolation of each anhydride so it was removed at this stage. Acidification of the alkaline solution gave a mixture of dicarboxylic acids. Without further purification, refluxing the mixture in acetic anhydride for 12 h resulted in formation of the *trans,cis*-anhydride (IX) in good yield. Stereochemical assignment of the anhydrides (VII)—(IX) was provided by the synthesis of the lycoranes.

Treatment of the anhydride (IX) with methanol in benzene gave a mixture of the half-esters (X) and (XI) in 7 : 3 ratio. The major one (X) was converted into the lactam-ester (XIV) by treatment with thionyl chloride followed by sodium azide to give the azide (XII) which was subjected to Curtius rearrangement in ben-

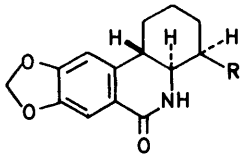
zene to give the isocyanate (XIII). Attempts to cyclise the isocyanate (XIII) to the lactam-ester (XIV) with trifluoroacetic acid, which had been applied to the synthesis of heamanthidine,[6] were unsuccessul. Eventually,



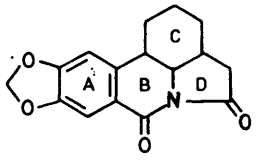
(XIV) R = CO_2Me
(XV) R = CH_2OH
(XVI) R = CH_2OTs



(XVII)



(XVIII) R = CO_2Me
(XIX) R = CH_2OH
(XX) R = CH_2OTs
(XXI) R = CH_2CN



(XXII) BC *trans*, CD *cis*
(XXIX) BC *trans*, CD *trans*

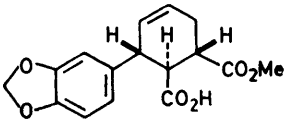
we found that tin(IV) or titanium(IV) chloride afforded good results, yielding the lactam-ester (XIV) in 64% yield starting from the half-ester (X).

Attempts at partial reduction of the ester function of the lactam-ester (XIV) with lithium aluminium hydride in tetrahydrofuran gave a mixture (t.l.c.). However, reduction of the mixture with sodium borohydride afforded the lactam-alcohol (XV) in low yield. Based on this result, reduction of the lactam-ester (XIV) with lithium aluminium hydride in tetrahydrofuran at −78° followed by sodium borohydride at −5 to 0° furnished the lactam-alcohol (XV) (88%) which showed a carbonyl band at 1 660 cm^{-1} in the i.r. spectrum, confirming the structure.

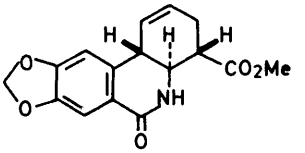
The lactam-alcohol (XV) was easily converted to the tosylate (XVI) which, surprisingly, gave the *cis,cis*-lactam-nitrile (XVII)[3] by cyanation with potassium cyanide in dimethyl sulphoxide. This indicates that the 10b-position had the character of an active methine, and was sensitive to base, giving the lactam (XVII) with a *cis,cis* ring juncture. In order to mitigate this susceptibility, the olefinic bond in ring C of the lactam-ester (XIV) was hydrogenated. The resulting dihydrolactam-ester (XVIII) was subjected to reduction with lithium aluminium hydride followed by sodium borohydride in the same manner as above to give the dihydrolactam-alcohol (XIX), which was converted to the tosylate (XX) in the usual manner. Treatment of the tosylate (XX) with potassium cyanide in dimethyl sulphoxide gave the nitrile (XXI) in good yield.

Hydrolysis of the nitrile (XXI) with concentrated hydrochloric acid followed by treatment with acetic anhydride afforded the imide (XXII), the structure of which was confirmed by its mass (virtually identical with that of the previously synthesised *cis,cis*-imide[3]) and i.r. spectra (1 750 and 1 660 cm^{-1}). Lithium aluminium hydride reduction of the imide in tetrahydrofuran gave (±)-α-lycorane (I), m.p. 92—93°, the i.r. spectrum of which was superimposable upon that of the authentic specimen.

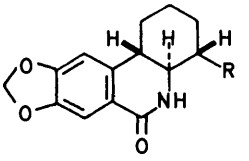
β-Lycorane was synthesised from anhydride (VII), obtained from the Diels–Alder cycloaddition of the alcohol (V) and fumaric acid, by the same sequence of reactions used for the synthesis of α-lycorane. This confirmed, in turn, the stereostructure of the anhydride (VII). Thus, treatment of the anhydride (VII) with methanol gave the half-ester (XXIII). The same reaction sequence, chlorination, azide formation, rearrangement, and cyclisation with tin(IV) chloride furnished the lactam-ester (XXIV), hydrogenation of which gave the dihydrolactam-ester (XXV). Reduction of the dihydrolactam (XXV) with lithium aluminium hydride followed by sodium borohydride gave the lactam-alcohol (XXVI) in good yield. Tosylation of the alcohol (XXVI) followed by cyanation gave the lactam-nitrile (XXVIII), which was converted into the imide (XXIX) in the same way as for the *trans,cis*-nitrile (XXI). Lithium aluminium hydride reduction of the imide (XXIX) completed the synthesis of (±)-β-lycorane (II),



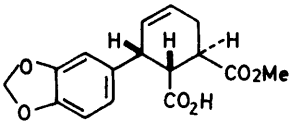
(XXIII)



(XXIV)



(XXV) R = CO_2Me
(XXVI) R = CH_2OH
(XXVII) R = CH_2OTs
(XXVIII) R = CH_2CN



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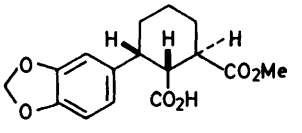
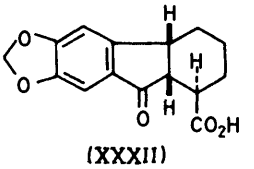


(XXXI)



(XXXII)

the i.r. spectrum of which was identical with that of the authentic specimen of β-lycorane.[2]

Anhydride (VIII) was not identical with compounds (VI), (VII), and (IX), suggesting the stereostructure to be *cis,trans*. Methanolysis of the anhydride (VIII)

gave the half-ester (XXX) in 80% yield, hydrogenation of which gave the dihydro-half-ester (XXXI). Friedel–Crafts cyclisation of the dihydro-half-ester (XXXI) with phosphorus(v) chloride followed by tin(IV) chloride in methylene chloride afforded the hexahydrofluorenone (XXXII). The fluorenone (XXXII) was identical in all respects with the compound [1] synthesised and converted into (±)-δ-lycorane (IV), completing the stereoselective synthesis of the stereoisomeric lycoranes from anhydrides (VII)—(IX).

EXPERIMENTAL

M.p.s were determined with a Yanagimoto microscope hot stage apparatus. I.r. spectra were recorded with a Hitachi model 215 spectrophotometer and mass spectra were with a Hitachi RMU-6D mass spectrometer with a direct heated inlet system.

trans,trans- (VII) *and* cis,trans-*Anhydride* (VIII).—A solution of 1-(3,4-methylenedioxyphenyl)but-3-en-1-ol (V) [prepared from piperonal (10 g), allyl chloride (6 g), and magnesium (2.5 g) [3]] and fumaric acid (6.5 g) in acetic anhydride (120 ml) was heated under reflux for 4 h. After removal of the solvent under reduced pressure, the residue was taken up in ethyl acetate and ethyl acetate insoluble material was removed by filtration. The filtrate was washed with aqueous sodium carbonate and water, dried, and evaporated to dryness to leave a crystalline residue (10 g). Repeated fractional recrystallisation of the residue from benzene gave the trans,trans-3-(3,4-*methylenedioxyphenyl*)-1,2,3,6-*tetrahydrophthalic anhydride* (VII) (1 g) as needles, m.p. 144—146° (Found: C, 66.3; H, 4.4. $C_{15}H_{12}O_5$ requires C, 66.2; H, 4.4%), $\nu_{max.}$ (KBr) 1 860 and 1 790 cm^{-1} (CO), and the cis,trans-*anhydride* (VIII) (1 g) as needles, m.p. 158—169° (Found: C, 66.3; H, 4.6%), $\nu_{max.}$ (KBr) 1 855 and 1 785 cm^{-1} (CO). The mother liquor was concentrated to dryness to give a gummy residue which was chromatographed on silica gel with chloroform. The first eluate gave a tarry residue which was not investigated further. The second eluate gave the *trans,cis*-anhydride (IX) (50 mg). Subsequent elution gave a mixture of the anhydrides (VII) and (VIII).

trans,cis-*Anhydride* (IX).—The anhydride mixture obtained from the Diels–Alder reaction [from piperonal (50 g)] was heated under reflux in 4% aqueous sodium hydroxide (500 ml) for 1 h. An insoluble gum was removed by filtration, and the filtrate was washed with ether and acidified with concentrated hydrochloric acid. The precipitate was heated under reflux in acetic anhydride (800 ml) for 12 h. The solution was concentrated to *ca.* 200 ml, diluted with acetic acid (200 ml) and decolourised with Norit. After removal of Norit by filtration, the filtrate was concentrated to dryness to leave the trans,cis-*anhydride* (IX) (25 g) as needles, m.p. 136—137° (from benzene), (Found: C, 66.2; H, 4.4%), $\nu_{max.}$ (KBr) 1 850 and 1 775 cm^{-1} (CO).

Conversion of Anhydrides (VII) *and* (VIII) *into Anhydride* (IX).—The *trans,trans-* or *cis,trans*-anhydride (VII) (500 mg) was heated under reflux in acetic anhydride (30 ml) for 12 h. Removal of the solvent followed by recrystallisation from benzene gave the *trans,cis*-anhydride (IX) (400 mg).

Methanolysis of trans,cis-*Anhydride* (IX).—A suspension of the *trans,cis*-anhydride (IX) (29 g) in benzene (600 ml), methanol (15 ml), and pyridine (5 ml) was stirred at room temperature for 3 h to give a clear solution. The solution was washed with dilute hydrochloric acid, water, and aqueous sodium carbonate. The alkaline washing was acidified with concentrated hydrochloric acid and extracted with methylene chloride. The extract was washed with water, dried, and concentrated to dryness to leave a residue which crystallised from methanol. Fractional recrystallisation from the same solvent gave *methyl hydrogen* 6-(3,4-*methylenedioxyphenyl*)-1,2,3,6-*dihydrophthalate* (X) as prisms, m.p. 168—169° (Found: C, 63.2; H, 5.2. $C_{16}H_{16}O_6$ requires C, 63.2; H, 5.3%). From the mother liquor, the isomeric *half-ester* (XI) was crystallised from methanol as prisms, m.p. 151—152° (Found: C, 63.1; H, 5.3%).

trans,cis-*Lactam-ester* (XIV).—The *trans,cis*-half-ester (XI) (2 g) was treated with thionyl chloride (3 ml) in benzene (10 ml) under reflux for 1 h. The mixture was evaporated under reduced pressure to give a residue which was taken up in acetone (10 ml). The solution was added dropwise to a solution of sodium azide (1 g) in water (3 ml) with stirring. The whole was stirred with ice–salt cooling for 1.5 h, diluted with water, and extracted with benzene (200 ml). The extract was washed with brine, dried, and filtered. The filtrate was heated under reflux for 2 h and evaporated under reduced pressure to give a residue which was taken up in methylene chloride (25 ml). Tin(IV) chloride (3 ml) was added to the methylene chloride solution with stirring at room temperature, and stirring was continued overnight. The mixture was diluted with methylene chloride and washed with dilute hydrochloric acid and water, and dried. Removal of the solvent gave *methyl* 8,9-*methylenedioxy*-6-*oxo*-3,4,4a,5,6,10b-*hexahydrophenanthridine*-4-*carboxylate* (1.3 g) which crystallised from ethanol as prisms, m.p. 192—194° (Found: C, 63.7; H, 5.0; N, 4.6. $C_{16}H_{15}NO_5$ requires C, 63.8; H, 5.0; N, 4.7%), $\nu_{max.}$ (Nujol) 3 160 (NH), 1 735, and 1 665 cm^{-1} (CO).

trans,cis-*Dihydrolactam-ester* (XVIII).—The lactam (XIV) (1 g) was hydrogenated in acetic acid with platinum oxide as catalyst. The usual work-up gave the *lactam* (XVIII) (650 mg) which crystallised from acetic acid as needles, m.p. 192—194° (Found: C, 63.2; H, 5.7; N, 4.5. $C_{16}H_{17}NO_5$ requires C, 63.4; H, 5.7; N, 4.6%), $\nu_{max.}$ (KBr) 3 165 (NH), 1 730, and 1 665 cm^{-1} (CO).

trans,cis-*Dihydrolactam-alcohol* (XIX).—A solution of the lactam (XVIII) (150 mg) and lithium aluminium hydride (30 mg) in tetrahydrofuran (15 ml) was stirred at −78° under nitrogen for 30 min, at −20° for 30 min, and at 0° for 15 min. The whole was again cooled at −78° and lithium aluminium hydride (10 mg) was added to the mixture and warmed at 0°. The mixture was treated with water, sodium borohydride (150 mg) was added to the mixture, and the whole was stirred at room temperature for 15 min. The mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with dilute hydrochloric acid and water and dried. Removal of the solvent gave the *lactam-alcohol* (XIX) (120 mg) which crystallised from ethanol as needles, m.p. 250—254° (Found: C, 65.4; H, 6.2; N, 5.1. $C_{15}H_{17}NO_4$ requires C, 65.4; H, 6.2; N, 5.1%), $\nu_{max.}$ (Nujol) 3 230, 3 130 (OH and NH), and 1 660 cm^{-1} (CO).

Tosylation of the Dihydrolactam-alcohol (XXI).—The dihydrolactam-alcohol (XIX) (100 mg) was treated with tosyl chloride (150 mg) in pyridine (8 ml) at room temperature overnight. The usual work-up gave the *tosylate* (XX) which crystallised from ethanol as prisms, m.p. 233—238° (Found: M^+, 429. $C_{22}H_{23}NO_6S$ requires M, 429), $\nu_{max.}$ (KBr) 3 120 (NH) and 1 630 cm^{-1} (CO).

Cyanation of the Tosylate (XX).—A mixture of the tosylate (XX) (50 mg), potassium cyanide (100 mg), and dimethyl sulphoxide (8 ml) was heated with stirring at 70° overnight. After removal of the solvent under reduced pressure, the residue was diluted with water and extracted with chloroform. The extract was washed with water, dried, and evaporated to dryness to give a residue which was chromatographed on silica gel in chloroform. Elution with chloroform gave the *nitrile* (XXI) (24 mg) which crystallised from ethanol as needles, m.p. 293—299° (Found: C, 67.4; H, 5.5; N, 9.7. $C_{16}H_{16}N_2O_3$ requires C, 67.6; H, 5.7; N, 9.9%), $\nu_{max.}$ (KBr) 3 120 (NH), 2 220 (CN), and 1 658 cm^{-1} (CO).

trans,cis-*Imide* (XXII).—The nitrile (XXI) (23 mg) was treated with concentrated hydrochloric acid (4 ml) and acetic acid (4 ml) on a water-bath for 2 h. The mixture was concentrated under reduced pressure to leave a residue which was heated in acetic anhydride (8 ml) on a water-bath for 1.5 h. Removal of the solvent gave the *imide* (XXII) which crystallised from ethanol as needles, m.p. 217—221° (Found: C, 67.2; H, 5.4; N, 4.7. $C_{16}H_{15}NO_4$ requires C, 67.4; H, 5.3; N, 4.9%), $\nu_{max.}$ (KBr) 1 750 and 1 660 cm^{-1} (CO).

(±)-α-*Lycorane* (I).—A solution of the imide (XXII) (30 mg) and lithium aluminium hydride (50 mg) in tetrahydrofuran (10 ml) was heated under reflux for 2 h. The usual work-up gave a residue which was chromatographed on alumina in benzene. Elution with the same solvent gave (±)-α-lycorane (I) (10 mg) which crystallised from benzene–hexane as prisms, m.p. 92—93° (lit., 93—94°). The synthetic sample showed i.r. and n.m.r. spectra identical with those of an authentic sample.

trans,trans-*Half-ester* (XXIII).—The *trans,trans*-anhydride (VII) (12 g) was treated with methanol in the same manner as mentioned for the *trans,cis*-anhydride (IX) to give the trans,trans-*half-ester* (XXIII) (8 g) which crystallised from ethyl acetate as plates, m.p. 179—183° (Found: C, 62.9; H, 5.2. $C_{16}H_{16}O_6$ requires C, 63.2; H, 5.3%), $\nu_{max.}$ (KBr) 1 740 and 1 690 cm^{-1} (CO).

trans,trans-*Lactam-ester* (XXIV).—The *trans,trans*-half-ester (XXIII) (2 g) was subjected to the same reaction sequence as for preparation of the *trans,cis*-lactam-ester (XIV) to give the *lactam-ester* (XXIV) which crystallised from dioxan, m.p. 242—245° (Found: C, 63.5; H, 4.8; N, 4.7. $C_{16}H_{15}NO_5$ requires C, 63.8; H, 5.0; N, 4.7%). $\nu_{max.}$ (Nujol) 3 170 (NH), 1 730, and 1 660 cm^{-1} (CO). Hydrogenation of the lactam (XXIV) (2 g) in the same manner as for the lactam (XVIII) gave the *lactam-ester* (XXV) (1.4 g) which crystallised from ethanol as needles, m.p. 223—229° (Found: C, 63.4; H, 5.4; N, 4.4. $C_{16}H_{17}NO_5$ requires C, 63.4; H, 5.7; N, 4.6%); $\nu_{max.}$ (Nujol) 3 170 (NH), 1 730, and 1 680 cm^{-1} (CO).

trans,trans-*Dihydrolactam-alcohol* (XXVI).—The lactam-ester (XXV) (900 mg) was treated with lithium aluminium hydride followed by sodium borohydride in the same way as for the *trans,cis*-lactam-ester (XVIII) to give the trans,trans-*lactam-alcohol* (XXVI) (720 mg) which crystallised from ethanol as plates, m.p. 248—252° (Found: C, 65.4; H, 6.4; N, 5.1. $C_{15}H_{17}NO_4$ requires C, 65.4; H, 6.2; N, 5.1%), $\nu_{max.}$ (Nujol) 3 230, 3 150 (NH and OH), and 1 650 cm^{-1} (CO).

Tosylation of the Alcohol (XXVI).—A solution of the alcohol (XXVI) (700 mg) and tosyl chloride (1 g) in pyridine (50 ml) was left at room temperature overnight. The usual work-up gave the *tosylate* (XXVII) (700 mg), which crystallised from ethanol–chloroform as plates, m.p. 234—238° (Found: M^+, 429. $C_{22}H_{23}NO_6S$ requires M^+, 429), $\nu_{max.}$ (Nujol) 3 160 (NH) and 1 665 cm^{-1} (CO).

trans,trans-*Dihydrolactam-nitrile* (XXVIII).—The tosylate (XXVII) (750 mg) was treated with potassium cyanide (750 mg) in dimethyl sulphoxide (75 ml) in the same manner as for the *trans,cis*-tosylate (XX) to give the *nitrile* (XXVIII) (350 mg) which crystallised from acetic acid as plates, m.p. 318—322° (Found: C, 67.5; H, 5.4; N, 9.8. $C_{16}H_{16}N_2O_3$ requires C, 67.6; H, 5.7; N, 9.9%), $\nu_{max.}$ (KBr) 3 170 (NH), 2 270 (CN), and 1 665 cm^{-1} (CO).

trans,trans-*Imide* (XXIX).—A solution of the nitrile (XXVIII) in concentrated hydrochloric acid (15 ml) and acetic acid (15 ml) was heated on a water-bath for 2 h. After removal of the solvent, the residue was heated in acetic anhydride (15 ml) for 10 h. The same work-up for the *trans,cis*-imide (XXII) gave the *trans,trans*-imide (XXIX) (360 mg) which crystallised from ethanol as needles, m.p. 237—240° (Found: C, 67.2; H, 5.4; N, 4.6. $C_{16}H_{15}NO_4$ requires C, 67.4; H, 5.3; N, 4.9%), $\nu_{max.}$ (KBr) 1 760 and 1 668 cm^{-1} (CO).

(±)-β-*Lycorane* (II).—A solution of the imide (XXIX) (310 mg) in tetrahydrofuran (50 ml) was added dropwise to a suspended solution of lithium aluminium hydride (300 mg) in tetrahydrofuran (30 ml), and the whole was heated under reflux with stirring for 2 h. The usual work-up gave a residue which was chromatographed on alumina in benzene. Elution with benzene–chloroform (10 : 1) gave (±)-β-lycorane (II) (65 mg) which crystallised from pentane as prisms, m.p. 87—90°; the i.r. spectrum was identical with that of an authentic sample.

cis,trans-*Half-ester* (XXX).—A solution of the anhydride (VIII) (500 mg) in methanol (1 ml), benzene (20 ml), and pyridine (1 ml) was stirred at room temperature for 3 h. The same work-up as for the *trans,cis*- and *trans,trans*-half-esters (XI) and (XIV) gave the *cis,trans*-half-ester (XXX) (300 mg) which crystallised from methanol as needles, m.p. 194—196° (Found: C, 60.3; H, 5.8. $C_{16}H_{16}O_6,4/5H_2O$ requires C, 60.2; H, 5.6%). Hydrogenation of the half-ester (XXX) (250 mg) in ethanol gave the *dihydro-half-ester* (XXXI) (240 mg) as an oil (Found: M^+, 306. $C_{16}H_{18}O_6$ requires M^+, 306), $\nu_{max.}$ ($CHCl_3$) 1 710 and 1 690 cm^{-1} (CO).

Friedel–Crafts Cyclisation of Half-ester (XXXI).—Phosphorus(v) chloride (80 mg) was added to a solution of the half-ester (XXXI) (120 mg) in methylene chloride (10 ml) and the whole was stirred at room temperatire for 1 h. Tin(IV) chloride (0.5 ml) was added to the solution and stirred under ice-cooling for 30 min. The solution was diluted with methylene chloride and washed with dilute hydrochloric acid, aqueous sodium carbonate, and water, and dried. Removal of the solvent left the fluorenone (XXXII) which crystallised from ethanol–ether as prisms and was identical in all respects with an authentic sample prepared previously and transformed to δ-lycorane.[1]

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