Natural and Synthetic Pyrrol-2-ylpolyenes

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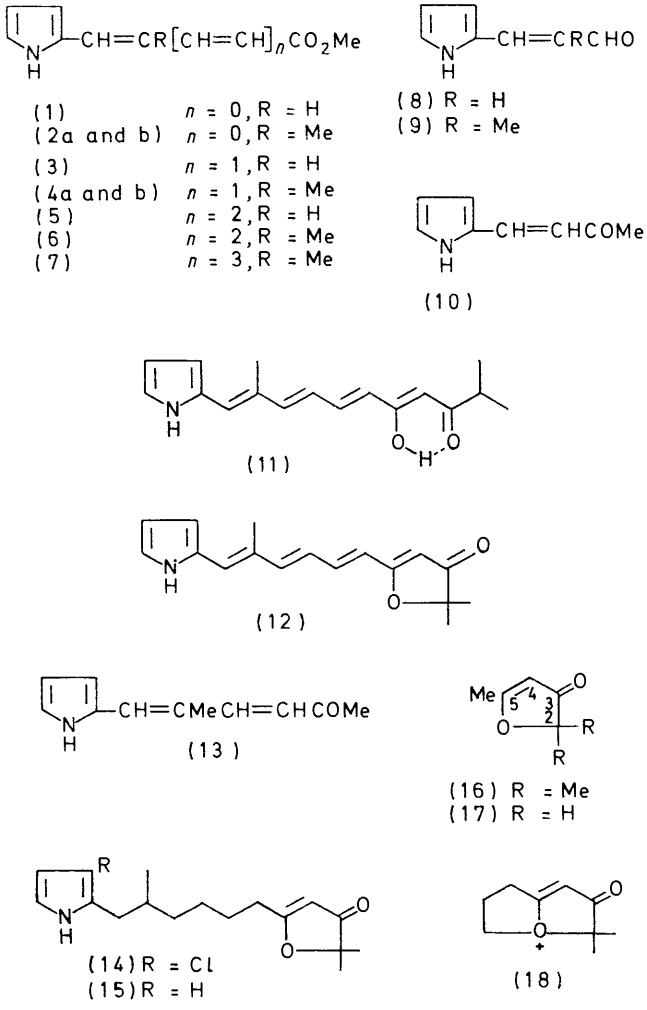
By structural studies, and comparisons with synthetic models, the two main pigments of *Wallemia sebi* have been identified as 2,10-dimethyl-5-hydroxy-11-(pyrrol-2-yl)undeca-4,6,8,10-tetraen-3-one (11) and 2,2-dimethyl-5-[5-methyl-6-(pyrrol-2-yl)hexa-1,3,5-trienyl]furan-3(2*H*)-one (12). Geometrical isomers and chloro-derivatives of these pigments were also observed.

THE fungus imperfectus, *Wallemia sebi* (Fr.) v. Arx,[1] was first reported in 1832.[2] A strain of this bright



orange fungus was isolated from bee combs and identified by the Commonwealth Mycological Institute, where it has accession number [M]140630. The organism for our studies was grown on solid medium. Extraction of the fungus with methanol, followed by chromatography, yielded six pigments. These compounds appear to be the first natural pyrrol-2-ylpolyenes to be reported, though monopyrroles substituted in the 2-position, while rare, are not unknown.[3-5]

The major pigment, 'wallemia A', $C_{17}H_{21}NO_2$, crystallises as orange needles, m.p. 107° (from cyclohexane). We formulate it as (11). The second most abundant pigment, 'wallemia C', $C_{17}H_{19}NO_2$, crystallises as orange prisms, m.p. 206—208° (from chloroform–cyclohexane). We suggest for it the structure (12). The other pigments are geometrical isomers (B and D) or chloro-derivatives (E and F) of wallemia A and C. The evidence for these various structural assignments is presented later in this paper.

Synthesis of Model Compounds.—There are few examples [6,7] of polyunsaturated 2-substituted pyrroles in the literature outside the porphyrin and corrin fields. As models for our studies we have synthesised a series of such compounds by Wittig condensations of the appropriate phosphoranes with pyrrole carbaldehydes.

Condensation of 2-formylpyrrole with methoxycarbonylmethylenetriphenylphosphorane in benzene gave the enoate (1). (The corresponding ethyl ester has previously been reported.[6]) Its n.m.r. spectrum contained a pair of doublets attributable to the α- and β-protons; their coupling constant (J 16 Hz) showed that (1) has the *trans*(*E*)-configuration.

Reaction of 2-formylpyrrole under the same conditions with α-methoxycarbonylethylidenetriphenylphosphorane,[8] gave the α-methyl derivative (2a), but the condensation between the aldehyde and the parent Wittig salt, α-methoxycarbonylethyltriphenylphosphonium bromide,[8] in 1,2-epoxybutane [9] gave a mixture of (2a) and, as a minor product, its geometrical isomer (2b). On irradiation with u.v. light (2b) was readily converted into (2a). The more stable isomer (2a) was assigned the *trans*(*E*)-configuration as the chemical shift of the β-proton in its n.m.r. spectrum was almost identical with

[1] J. A. von Arx, 'The Genera of Fungi Sporulating in Pure Culture,' Stechart-Hafner Service Agency, New York, 1970, p. 166.
[2] Named *Sporendonema sebi* by Fries, *Syst. Mycol.*, 1832, **3**, 434.
[3] A. J. Birch, P. Hodge, R. W. Rickards, R. Takeda, and T. R. Watson, *J. Chem. Soc.*, 1964, 2641.
[4] E. Fetz and C. Tamm, *Helv. Chim. Acta*, 1966, **49**, 349.
[5] S. S. Hanessian and J. S. Kaltenbrown, *J. Amer. Chem. Soc.*, 1956, **88**, 5409.
[6] R. A. Jones and J. A. Lindner, *Austral. J. Chem.*, 1965, **18**, 875.
[7] E. Lubrzynsk, *J. Chem. Soc.*, 1916, 1118.
[8] O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, 1957, **40**, 1242.
[9] D. E. Loeber, S. W. Russell, T. P. Toube, B. C. L. Weedon, and J. Diment, *J. Chem. Soc.* (*C*), 1971, 404.

that of the β-proton in (1). The corresponding signal for (2b) was 0·80 p.p.m. further upfield; similar differences have been observed between the signals for the β-proton in other αβ-unsaturated esters.[10]

Reaction of 2-formylpyrrole with 3-methoxycarbonylprop-2-enylidenetriphenylphosphorane [11] in benzene gave the dienoate (3) as a mixture of stereoisomers. Careful crystallisation from ether and cyclohexane at 0° gave one of these isomers as a crystalline yellow solid, m.p. 130°. However, at room temperature the material rapidly reverted to the original isomer mixture.

Bestmann [12] has reported the alkylation of certain phosphoranes by alkyl halides. Treatment of the preceding phosphorane with methyl iodide in refluxing ethyl acetate precipitated crystalline 3-methoxycarbonyl-1-methylprop-2-enyltriphenylphosphonium iodide. The phosphorane prepared from this Wittig salt by reaction with base was condensed with 2-formylpyrrole to yield methyl 4-methyl-5-(pyrrol-2-yl)penta-2,4-dienoate as a mixture of stereoisomers from which the major isomer (4a) was isolated by careful crystallisation. This isomer appears to have a *cis*(*Z*)-2-configuration. The n.m.r. spectrum shows a doublet (*J* 8·6 Hz further split by small couplings) at δ 7·32, clearly the signal for 3-H on a *cis*-αβ-unsaturated double bond.

The trienoate (5) was similarly synthesised by the condensation of 2-formylpyrrole with the freshly prepared phosphorane from 6-methoxycarbonylpenta-2,4-dienyltriphenylphosphonium bromide, itself the product of the reaction of methyl 6-bromosorbate [13] with triphenylphosphine. However, treatment of the phosphorane with methyl iodide under the conditions [12] used for the phosphorane derived from methyl 4-bromocrotonate, in an attempt to develop an analogous synthesis for the methylated trienoate (6), failed to yield the desired Wittig salt. The n.m.r. spectrum of the crystalline product lacked a signal for the expected methyl group and the material was not investigated further.

An alternative route to (6) was therefore devised. Treatment of 2-formylpyrrole with formylethylidenetriphenylphosphorane [14] gave 2-methyl-3-(pyrrol-2-yl)prop-2-enal (9). Condensation of this aldehyde with 3-methoxycarbonylprop-2-enylidenetriphenylphosphorane [11] yielded (6).

The reaction between the same aldehyde (9) and methoxycarbonylmethylenetriphenylphosphorane [8] gave in good yield an isomer (4b) of the dienoate (4a). This isomer is *trans* about the 2,3-double bond. 2- and 3-H appear in the n.m.r. spectrum as a pair of doublets at δ 5·86 and 7·42, respectively, with a mutual *trans*-coupling of 16 Hz. The two isomers could not be interconverted by irradiation with u.v. light. Their mass spectra were identical. We comment on their stereochemistry about the 4,5-double bond later.

The tetraenoate (7) was synthesised by the same route from the aldehyde (9) and the freshly prepared phosphorane from 6-methoxycarbonylpenta-2,4-dienyltriphenylphosphonium bromide.

Other model compounds prepared in the present study were 3-(pyrrol-2-yl)prop-2-enal (8) (from the reaction of 2-formylpyrrole and formylmethylenetriphenylphosphorane [14]), 4-(pyrrol-2-yl)but-3-en-2-one [15] (10) (by the aldol condensation between 2-formylpyrrole and acetone), and 5-methyl-6-(pyrrol-2-yl)hexa-3,5-dien-2-one (13) [by the aldol condensation of the aldehyde (9) with acetone].

Examination of the chemical shift of the *C*-methyl resonances in the n.m.r. spectra of the model compounds (2a and b), (4a and b), (6), (7), (9), and (13) (Table 1) throws further light on their stereochemistry.

TABLE 1

The chemical shifts [δ (p.p.m.) from Me_4Si] of the vinyl methyl groups in the n.m.r. spectra of some pyrrolylpolyenes

Compound	δ (Me)	Compound	δ (Me)
(2a)	2·18	(7)	2·10
(2b)	2·06	(9)	2·17
(4a)	1·97	(11)	1·94
(4b)	2·07	(12)	2·00
(6)	2·07	(13)	2·10

The *C*-methyl signal of the *trans*(*E*)-compound (2a) is 0·12 p.p.m. further downfield than the corresponding resonance of its *cis*(*Z*)-isomer (2b). The difference between the *C*-methyl shifts in the isomer pair (4a) and (4b) is 0·10 p.p.m. Comparison of the chemical shifts of the methyl signals of all the compounds derived from (9) [*viz.* (4b), (6), (7), and (13)] shows that they all lie in the range δ 2·07—2·10 and so probably retain the stereochemistry about the methylated double bond. The methyl protons in (2a and b) appeared relatively further downfield as they are deshielded by the adjacent ester function.

The u.v. light absorption data for this series of compounds are summarised in Table 2. The *trans*(*E*)-enoate (2a) has a similar extinction coefficient to that of the unmethylated analogue (1), but its absorption maximum is at a shorter wavelength. We attribute this difference to steric interaction between the *C*-methyl group and the adjacent hydrogen atoms on the pyrrole ring; this strain can only be relieved by the enoate system twisting out of the plane of the ring with a consequent restriction in the degree of overlap of the π orbitals of the ring and those of the enoate system. The *cis*(*Z*)-isomer (2b) absorbs at longer wavelengths, but with lower intensity.

In the dienoates, the in-chain methyl group has little effect on the extinction coefficient, but the auxochromic effect of the group on the wavelength appears to be

[10] L. M. Jackman and S. Sternhall, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 185.
[11] E. Bucht and F. Andrée, *Chem. Ber.*, 1959, **92**, 3111.
[12] H. J. Bestmann and H. Schultz, *Chem. Ber.*, 1962, **95**, 2921.
[13] I. Heilbron, E. R. H. Jones, and D. G. O'Sullivan, *J. Chem. Soc.*, 1946, 866.
[14] S. Trippet and D. M. Walker, *J. Chem. Soc.*, 1961, 1226.
[15] R. A. Jones and J. A. Lindner, *Austral. J. Chem.*, 1965, **18**, 877.

exactly balanced (4a), or even reversed (4b), by the steric effects.

Comparison of the maxima for (5) and (6) indicates that the in-chain methyl group has little effect on either the wavelength or intensity of the absorption.

TABLE 2

The principal absorption maxima in the electronic spectra of A, some pyrrolylpolyenes and B, their reduction products

Compound	$\lambda_{max.}$/nm (10^{-3} ε) A [a]	B [b]
(1)	331 (25·7)	
(2a)	325 (25·5)	271 [a]
(2b)	335 (15·0)	
(3)	368 (34·5)	317
(4a)	368 (34·0)	319
(4b)	364 (34·0)	312
(5)	394 (43·6)	342
(6)	393 (41·5)	340
(7)	409 (43·2)	366
(8)	350	
(9)	345 (30·5)	
(10)	348	
(11)	425 (49·3)	347 [c]
(12)	431 (41·0)	348
(13)	382	312 [c]

[a] In ethanol. [b] Lithium aluminium hydride reduction products, in benzene, unless indicated to the contrary. [c] Sodium borohydride used for reduction.

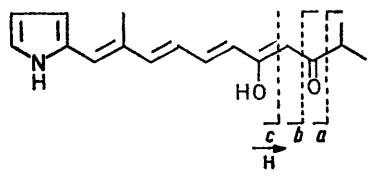
Reduction of the model compounds with lithium aluminium hydride produced highly unstable allylic alcohols. The absorption maxima in the electronic spectra of the crude reduction products are recorded in Table 2. The position of the maximum for reduced (4b) is 7 nm to lower wavelength than that of reduced (4a), suggesting that there is also a difference in stereochemistry about the methylated double bond. Reduction of (13) with borohydride should give an alcohol with the same chromophore as reduced (4b), and the absorption maxima are in fact at the same wavelength. Reduction of (6), the vinylogue of (4b), gave a compound absorbing 28 nm to longer wavelength, while the additional double bond in the next member of the series, the reduction product of (7), produced an increment of 26 nm.

The Structure of Wallemia A.—We review the evidence for the various features of structure (11) separately.

(i) *The 2-substituted pyrrole.* In the n.m.r. spectrum of the pigment in deuteriochloroform there were three one-proton signals in the aromatic region at δ 6·22, 6·35, and 6·81. They were considerably sharpened after the solution had been shaken with deuterium oxide, and then showed couplings of 1·1, 2·6, and 3·6 Hz, in good agreement with those recorded [16,17] for the 3,5-, 4,5-, and 3,4-coupling constants in 2-substituted pyrroles. In addition, the chemical shifts of these protons were very similar to those of the pyrrole 4-, 3-, and 5-protons in the model compounds whose spectra all resembled that of wallemia A in this area. The similarity was particularly striking with (4a) in which these protons appeared at δ 6·22, 6·38, and 6·82 with coupling constants identical with those of the natural compound. The broad N–H signal at δ *ca.* 8·35 was eliminated by the above exchange with deuterium oxide.

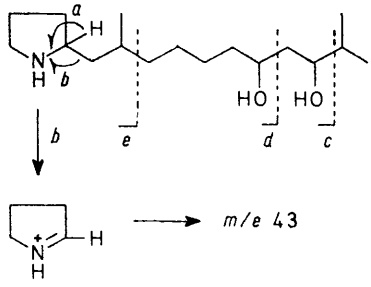
The presence of an N–H group could also be inferred from the i.r. spectrum, the broad absorption band at 3280 cm^{-1} due to the hydrogen-bonded N–H stretch in the solid phase sharpening and moving to 3480 cm^{-1} in solution. Other characteristic 2-substituted pyrrole [18] absorption bands in the spectrum were found at 1138 (N–H in-plane deformation), 1090 and 1033 (C–H in-plane deformations), and 882 cm^{-1} (C–H out-of-plane deformation).

Peaks in the low mass region of the mass spectrum (Scheme 1) of the natural product (*e.g.* *m/e* 80, C_5H_6N)



SCHEME 1

gave some indication of the presence of the heterocyclic portion of the molecule. However, the mass spectrum (Scheme 2) of perhydrowallemia A, obtained by hydro-



SCHEME 2

genation of wallemia A in ethanol over Adams catalyst, established the presence of the 2-substituted pyrrole group (fission *b*). The comparable intensity of the (*M* − 1) peak (fission *a*) relative to the molecular ion is characteristic of pyrrolidines.[19] Similar cleavages were observed in the mass spectrum of the pyrrolidine produced by hydrogenation of (7) over Adams catalyst.

(ii) *The isopropyl ketone.* The presence of an isopropyl group attached to a fully substituted sp^2 hybridised carbon atom in wallemia A was shown by the n.m.r. spectrum (six-proton doublet at δ 1·16 and one-proton septuplet at δ 2·54, showing a mutual coupling of 7 Hz at both 60 and 100 MHz).

[16] Ref. 10, p. 306.
[17] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, vol. 2, p. 788.
[18] R. A. Jones, *Austral. J. Chem.*, 1963, **16**, 93.
[19] H. Budzikiewicz, C. Djerassi, and D. H. Williams, ' Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967.

The mass spectra of both the pigment and its perhydro-derivative showed losses of 43 a.m.u. (Scheme 1, *a*, and Scheme 2, *c*, respectively). There was also a loss of 71 a.m.u., C_4H_7O by high resolution, from the molecular ion of wallemia A (Scheme 1, *b*), together with a peak at *m/e* 71 arising from the same cleavage, but with charge retention on the smaller fragment. The latter ion decomposes as expected by the expulsion of carbon monoxide (*m/e* 71 ⟶ 43, *m** 26·05).

(iii) *The enolic β-diketone.* The presence of a pH-sensitive chromophore in wallemia A was shown by a large hypsochromic shift of 15 nm in the position of the maximum in its electronic absorption spectrum upon addition of base. Furthermore the absorption maximum of the unstable crude sodium borohydride reduction product in methanol (Table 2) was 82 nm lower in wavelength than the parent compound, far too large a shift to be accounted for by the simple reduction of a conjugated or cross-conjugated ketone. The position of the main absorption band of the reduced material in benzene solution (347 nm) indicated the presence of a pyrrol-2-yltriene chromophore. Though the position of the light absorption maximum was 7 nm longer than that of the model prepared by reduction of (6), it was considerably shorter (18 nm) than that of the vinylogue obtained by reduction of (7). The difference between the maxima of reduced wallemia A and reduced (6) corresponds to that observed between the maxima of reduced (4a) and reduced (4b). This suggests that wallemia A has the opposite configuration about the double band adjacent to the pyrrole ring to that of the corresponding double bond in (6) and related compounds derived from (9).

In their n.m.r. spectra, enolic 1,3-dicarbonyl compounds [20a] show heavily deshielded enolic O–H signals at δ 12·3—16·7 whilst the olefinic 2-H lies between δ 5·5 and 7·1. The n.m.r. spectrum of wallemia A had a broad one-proton signal at δ 15·7 (removed by deuteriation) and a sharp one-proton resonance at δ 5·79. There is no doubt that an α-diketone is not present: such compounds' hydroxy-protons resonate [20b] further upfield (δ 5·27—8·75).

As expected, the strongly hydrogen-bonded carbonyl group has a lowered stretching frequency (1580 cm^{-1}) in the i.r. spectrum. The hydroxy-absorption band is at 3340 cm^{-1} in the solid phase and 3350 cm^{-1} in carbon tetrachloride solution.

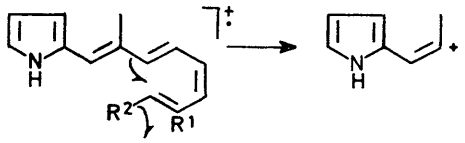
In the mass spectrum, perhydrowallemia A showed the fragmentations [21] (Scheme 2, *c* and *d*) of a 1,3-diol. Major fragments in the high mass region of the mass spectrum of the parent pigment (Scheme 1, *a*—*c*) corresponded to cleavages α to the two carbonyl groups.

These data are consistent with the presence of a completely enolic β-diketone at one end of the chromophore.

(v) *The vinylic methyl group.* The vinylic methyl protons gave rise to a signal at δ 1·94 in the n.m.r. spectrum of wallemia A. As the signals of three pyrrole ring protons were visible in the spectrum, the methyl group must lie in the polyene portion of the molecule.

The position of the methyl group is given by the mass spectrum of perhydrowallemia A. A prominent ion at *m/e* 112, $C_7H_{14}N$ by high resolution, corresponds to the cleavage shown (Scheme 2, *e*). The mass spectrum of the model pyrrolidine produced by hydrogenation of the tetraenoate (7) showed the same fragment.

Cleavage of the same bond in wallemia A itself gave rise to *m/e* 106, C_7H_8N by high resolution. However, this fragment was absent from the mass spectra of all the model compounds save (7), and we believe that it arises by a cyclic process (Scheme 3) similar to those postulated for fragmentation of other polyenes.



(7) R^1 = H, R^2 = CO_2Me
(11) R^1 = OH, R^2 = $COCHMe_2$

SCHEME 3

Comparison of the chemical shift (δ 1·94) of the vinylic methyl group in the n.m.r. spectrum of wallemia A with those of the model compounds (Table 1) supports the view that the double bond adjacent to the pyrrole ring has the opposite stereochemistry to that in (4b) and (6).

Wallemia C and F.—Wallemia C has the molecular formula $C_{17}H_{19}NO_2$ ($M^{+\cdot}$ at *m/e* 269). Prominent fragments in its mass spectrum at *m/e* 93 (C_6H_7N by high resolution) and *m/e* 80 (C_5H_6N) suggest the presence of a nitrogen heterocycle similar to that of wallemia A. The low field regions in the n.m.r. spectra also suggest a similarity between the two compounds. Wallemia C may thus be considered as a dehydrowallemia A.

The i.r. spectrum of wallemia C shows no hydroxy stretching frequency. The N–H absorption band is present (3490 cm^{-1} in carbon tetrachloride solution). Strong absorptions at 1676 (with a shoulder *ca.* 1690), 1580, and 1548 cm^{-1} suggest the presence of αβ-unsaturated ketone and/or enol ether or ester functions. In the n.m.r. spectrum of wallemia C, the signals due to the isopropyl ketone grouping in wallemia A are absent, and there is instead a six-proton singlet at δ 1·42, possibly a *gem*-dimethyl group. The vinylic methyl resonance is at δ 2·00, and the broad N–H signal (which is removed by deuteriation) appears at δ *ca.* 9. It is thus possible that wallemia C has the structure (12).

Reduction of wallemia C with lithium aluminium hydride for a few minutes gave a product with an absorption maximum in its u.v. spectrum at 375 nm, possibly corresponding to the chromophore of the reduced tetraenoate (7) (see Table 2) with an auxochromic oxygen substituent. Reduction for a longer period

[20] 'High Resolution N.M.R. Spectra Catalog,' Varian Associates, Palo Alto, 1963 (*a*) spectra nos. 185, 295, 316, 583, 600, 635, 656; (*b*) spectra nos. 129, 560, 647.
[21] Ref. 19, p. 106.

gave a product with a chromophore (Table 2) almost identical with that of the borohydride reduction product of wallemia A.

Wallemia C has not been obtained pure. Attempts to purify the samples merely concentrated the monochloro-derivative, wallemia F, $C_{17}H_{18}ClNO_2$.

Hydrogenation of the mixture of wallemia C and F under the conditions used to prepare perhydrowallemia A gave two main compounds which were separated by careful t.l.c. Their mass spectra show them to be hexahydro-derivatives of the chlorinated and non-chlorinated parent compounds, and we have assigned them the structures (14) and (15). The products have identical u.v. spectra, with maxima at 262 nm. The compounds (16) [22] and (17) [23] have maxima at 261 and 258 nm, respectively. The n.m.r. spectrum of the chloro-compound shows a six-proton singlet at δ 1·35 for a *gem*-dimethyl group, and a slightly broadened singlet at δ 5·30 for an olefinic proton. The 4-proton in (17) resonates at δ 5·41.[23] These data support the view that the molecule possesses a furan-3(2*H*)-one system. A prominent ion in the mass spectra of both compounds, *m/e* 153, must arise from an *a priori* unfavourable cleavage in the centre of the aliphatic chain. We postulate that a stable cyclic structure for this ion, such as (18), may explain its high relative abundance.

The mass spectra show that the pyrrole ring is unreduced. The base peak, *m/e* 80, of the unhalogenated molecule arises by cleavage at the position ' benzylic ' to the ring. In the chloro-compound the corresponding cleavage gives the halogenated (*m/e* 114/116) and unhalogenated (*m/e* 80) ions. Comparison of the mass spectra of the two hexahydro-derivatives thus establishes that the chlorine atom is at the pyrrole end of the molecule.

The signal in the n.m.r. spectrum for the vinylic methyl of wallemia C is replaced in its hexahydrochloro-derivative by a methyl doublet (*J* 6·5 Hz) at δ 1·19. The pyrrole ring gives rise to a broad NH absorption at δ *ca.* 7·8 and two one-proton triplets at δ 6·06 and 6·54 (*J ca.* 3 Hz). These are very similar to the signals for the 4- and 5-protons in 2,3-dimethylpyrrole [24] and 2-pentyl-3-methylpyrrole.[25] The chlorine atom may therefore be assigned to C(3) on the pyrrole ring.

Wallemia E.—The mass spectra of some samples of wallemia A show peaks due to wallemia E, a monochloro-derivative of A. We have not been able to isolate this compound. High resolution measurements on its molecular ion, *m/e* 305/307, show it to have the formula $C_{17}H_{20}ClNO_2$. Fragment ions at *m/e* 234/236, 220/222, and 140/142 confirm that it fragments in a similar fashion to the unhalogenated compound. We believe that it has the same gross structure as wallemia A, and in that case the chlorine atom must be located either on the pyrrole ring, or on the adjacent carbon, or (except for its apparent unreactivity) on the vinylic methyl group. It seems probable that the position of chlorination is the same as in wallemia F, *viz.* C(3) on the pyrrole ring.

Wallemia B and D.—Samples of wallemia A subjected to irradiation by u.v. light developed a peak for a *cis*-compound in their u.v. spectra at 308 nm, while the principal maximum in the visible region remained virtually unchanged. The *cis*-isomer thus formed, wallemia B, was also present in the crude pigment and could be separated from wallemia A by careful thin layer chromatography. It gave a single spot on t.l.c. but rapidly reverted to the equilibrium mixture, which contained 80% of wallemia A. As the methylated double bonds in the model compounds (4a) and (4b) do not undergo stereomutation under irradiation, wallemia B is likely to be *cis* at either the 6- or the 8-double bond. On steric grounds it seems probable that it is *cis*-6.

Similarly, wallemia C was associated with a material, wallemia D, responsible for an absorption band at 303 nm in the u.v. spectrum. However, wallemia D gave some indication on t.l.c. that it might not be a single compound. The interconversion of wallemia C and D was much more rapid than that of A and B, the equilibrium mixture at room temperature containing *ca.* 70% of wallemia C.

EXPERIMENTAL

Where appropriate, operations were carried out under nitrogen. Solvents were redistilled before use. Light petroleum refers to that fraction with b.p. 60—80° except where stated otherwise. M.p.s were determined on a Reichert heated-stage microscope and are uncorrected. Silica gel for t.l.c. was Kieselgel H unless otherwise indicated. Electronic spectra were recorded on a Unicam SP 800 instrument and i.r. spectra on Perkin-Elmer 257 or 225 spectrometers. N.m.r. spectra at 60 or 100 MHz were determined on Varian A60 or HA 100 spectrometers. Mass spectra were determined on an A.E.I. MS902 mass spectrometer; high resolution measurements were made relative to heptacosafluorotributylamine as reference. Selected peaks in spectra are quoted.

Growth and Extraction.—*Wallemia sebi* (Fr.) v. Arx [1] was grown on fifty plates containing Wickerham's medium [26] [yeast extract (3 g), malt extract (3 g), peptone (5 g), glucose (10 g), agar (20 g), and water (1 l)] in diffuse sunlight at room temperature for 14 days. (Direct sunlight was found to inhibit the growth of the fungus whilst the yield of pigment from cultures of the fungus which were grown in the dark was low.) At the end of this period the orange cultures had developed a green-brown colouration at the points of densest growth and the fungus covered about half the area of the plates. The fungus (52 g) was removed from the plates, pulverised with ether–methanol (1 : 1) (200 ml) for 15 min, filtered, and the filter cake was re-extracted with a further portion of ether–methanol (100 ml). The combined filtrate

[22] I. I. Nazarova, B. P. Gusev, and V. F. Kucherov, *Izvest. Akad. Nauk S.S.S.R.*, 1965, **70**, 729.
[23] A. Hofmann, W. v. Philipsborn, and C. H. Eugster, *Helv. Chim. Acta*, 1965, **48**, 1322.
[24] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1959, **37**, 1056.
[25] Ref. 20, spectrum no. 278.
[26] L. J. Wickerham, *Tech. Bull. U.S. Dept. Agric.*, 1951, **1029**, 1.

was dried ($MgSO_4$) and filtered and the solvent was evaporated under reduced pressure to yield a red gum. Column chromatography (silica gel, gradient elution with acetone in light petroleum) afforded two coloured fractions, which were further purified by t.l.c. (silica gel, 20% acetone in light petroleum) to give two crude pigments with R_F 0·7 and 0·3. The former was crystallised from a mixture of ether and cyclohexane to yield *wallemia A* [*2,10-dimethyl-5-hydroxy-11-(pyrrol-2-yl)undeca-4,6,8-tetraen-3-one*] (35 mg), m.p. 107°, $\lambda_{max.}$ (ethanol) 425 nm (ε 49,300), $\lambda_{max.}$ (ether) 420 nm, $\lambda_{max.}$ (light petroleum) 409 nm, $\nu_{max.}$ (KBr) 3340, 3280, 3100, 3030, 2970, 2930, 2870, 1580, 1480, 1445, 1415, 1380, 1360, 1320, 1300, 1255, 1215, 1165, 1123, 1095, 1030, 980, 935, 880, 790, 720, and 600 cm^{-1}, $\nu_{max.}$ (CCl_4) 3480, 3350, 3105, 3030, 2970, 2935, 2875, 1580, 1475, 1450, 1425, 1385, 1250, 1230, 1180, 1165, 1138, 1115, 1100, 1090, 1032, 980, 935, 882, and 710 cm^{-1}, δ ($CDCl_3$; 100 MHz) 1·16 (6H, d, *J* 7 Hz), 1·94 (3H, d, *J* 1·5 Hz), 2·54 (1H, m, *J* 7 Hz), 5·79 (1H, s), 6·22 (1H, m), 6·35 (1H, m), 6·81 (1H, m), 6·35—7·30 (5H), 8·35br (1H), and 15·75br (1H), *m/e* 271·154 (51%, $M^{+\bullet}$, $C_{17}H_{21}NO_2$ requires 271·157), 200·109 (25, $C_{13}H_{14}NO$ requires 200·107), 186·091 (7, $C_{12}H_{12}NO$ requires 186·091), 158·097 (21, $C_{11}H_{12}N$ requires 158·097), 133·065 (18, C_9H_9O requires 133·065), 106·065 (100, C_7H_8N requires 106·066), 93·034 (20, C_6H_5O requires 93·034), 80·049 (24, C_5H_6N requires 80·050), 43 (37), 41 (15), 39 (12), and 28 (30).

Treatment of the methanolic solution ($\lambda_{max.}$ 425 nm) of wallemia A containing a trace of acid with methanolic potassium hydroxide gave a solution with $\lambda_{max.}$ 410 nm.

The pigment was not acetylated on treatment with acetic anhydride in dry pyridine at room temperature in the dark for two days. Treatment with hexamethyldisilazane and trimethylchlorosilane in pyridine for one day failed to produce any trimethylsilylated derivative.

Repeated t.l.c. (silica gel, 25% acetone in benzene) of the more polar pigment yielded a mixture of wallemia C and wallemia F as a red solid (30 mg) which crystallised from cyclohexane and had m.p. 206—208°, $\lambda_{max.}$ (ethanol) 431 nm (ε 41,000), $\nu_{max.}$ (CCl_4) 3470, 3005, 2930, 2850, 1690infl, 1676, 1580, 1548, 1470, 1389, 1174, 1032, and 984 cm^{-1}, δ ($CDCl_3$; 100 MHz) 1·42 (6H), 2·00 (3H), 3·90 (*ca.* 1H), 5·60 (*ca.* 1H, m,), 6·00—7·60 (*ca.* 10H, complex m), and *ca.* 8·8br (1H), *m/e* 305 (15%), 304 (10), 303·106 (43, $M^{+\bullet}$ of wallemia F, $C_{17}H_{18}{}^{35}ClNO_2$ requires 303·103), 270 (24), 269·141 (100, $M^{+\bullet}$ of wallemia C, $C_{18}H_{19}NO_2$ requires 269·142), 268 (14), 254 (20), 226 (10), 217 (16), 202 (13), 199 (14), 198 (30), 197 (10), 184 (20), 183 (32), 182 (45), 181 (30), 180 (26), 168 (40), 176 (70), 157 (10), 156 (30), 154 (12), 130 (26), 127 (24), 117 (24), 115 (22), 114 (26), 93·059 (50, C_6H_7N requires 93·058), 80·051 (70, C_5H_6N requires 80·050), 77 (30), 67 (20), 65 (14), 55 (22), 43 (26), 41 (40), and 39 (32).

Attempted acetylation and trimethylsilylation under the same conditions as those used for wallemia A both failed. Treatment of the pigment with sodium borohydride in methanol yielded only starting material.

Reduction of Wallemia A with Sodium Borohydride.—Wallemia A (2 mg) in methanol (1 ml) was treated with sodium borohydride (20 mg). After the solution had been stirred for 15 min, dilute acetic acid (4N, 2 ml) was added. The solution was extracted with ether and the ethereal extracts were washed with saturated sodium hydrogen carbonate solution, then with water, and dried ($MgSO_4$). Filtration of the solution, and evaporation of the filtrate under reduced pressure, yielded the reduction product (1 mg), $\lambda_{max.}$ (ethanol) 343 nm, $\lambda_{max.}$ (benzene) 363, 347 (principal maximum), and 330infl nm. It was unstable and resisted further purification.

Perhydrowallemia A.—Wallemia A (8 mg) in ethanol (3 ml) was added to a previously hydrogenated suspension of Adams catalyst (10 mg) in ethanol (1 ml) and hydrogenated at room temperature and atmospheric pressure for 1 day. Filtration of the solution, and removal of the solvent under reduced pressure, gave a clear gum which exhibited only end absorption in the u.v. spectrum. The gum was purified by t.l.c. (silica gel, 30% ethanol in benzene containing 2% v/v of concentrated aqueous ammonia) to yield *perhydrowallemia A* as a clear oil (5 mg), *m/e* 285·267 (5%, $M^{+\bullet}$, $C_{17}H_{35}NO_2$ requires 285·267), 284·257 (4, *M* − 1, $C_{17}H_{34}NO_2$ requires 284·259), 242·212 (43, $C_{14}H_{28}NO_2$ requires 242·212), 224 (8), 198·185 (20, $C_{12}H_{24}NO$ requires 198·186), 169 (10), 112 (20), 109 (25), 97 (12), 96 (12), 93 (9), 81·071 (60, C_6H_9 requires 81·070), and 70·066 (100, C_4H_8N requires 70·066).

Reduction of Wallemia C and F with Lithium Aluminium Hydride.—A mixture of wallemia C and F (1 mg) in ether (2 ml) was added to lithium aluminium hydride (10 mg) in ether (5 ml). The mixture was stirred at room temperature for 5 min and water was then added. The mixture was extracted with ether and the extract was dried ($MgSO_4$) and evaporated to give a crude product (0·6 mg), $\lambda_{max.}$ (benzene) 375 nm, $\lambda_{max.}$ (ether) 368 nm. A similar reaction carried on for 30 min gave a product, $\lambda_{max.}$ (benzene) 348 nm, $\lambda_{max.}$ (ether) 344 nm.

Hydrogenation of Wallemia C and F.—A mixture of wallemia C and F (22 mg) in ethanol (5 ml) was hydrogenated over Adams catalyst (30 mg) in ethanol (5 ml) at room temperature and atmospheric pressure for 24 h. Filtration and evaporation of the solvent under reduced pressure gave an oil (29 mg). T.l.c. (silica gel HF, 20% acetone in light petroleum) followed by t.l.c. of the main band (silica gel HF, 15% acetone in light petroleum, repeated running) gave (i) *hexahydrowallemia C* (3 mg), $\lambda_{max.}$ (ethanol) 262 nm, *m/e* 275·189 (40%; $M^{+\bullet}$, $C_{17}H_{25}NO_2$ requires 275·189), 260 (1, *M* − Me), 195 (3), 192 (2), 153·091 (35, $C_9H_{13}O_2$ requires 153·092), 140 (8), 136 (7), 123 (6), 106 (5), 95 (3), 94 (17), 93 (8), 81 (20), 80·050 (100, C_5H_6N requires 80·050), 67 (6), 59 (2), 53 (11), 43 (6), and 41 (9) and (ii) *hexahydrowallemia F* (5 mg), $\lambda_{max.}$ (ethanol) 262 nm, δ ($CDCl_3$; 100 MHz) 1·19 (3H, d, *J* 6·5 Hz), 1·35 (6H, s), 1·2—1·8 (m), 2·45—2·7 (3H, m), 5·30 (1H, s), 6·06 (1H, t, *J* 3 Hz), 6·54 (1H, t, *J* 3 Hz), and *ca.* 7·8br (1H, removed by deuteriation); *m/e* 311 (13%), 310 (10), 309·150 (39, $M^{+\bullet}$, $C_{17}H_{24}{}^{35}ClNO_2$ requires 309·150), 275 (25), 274·180 (49, $C_{17}H_{24}NO_2$ requires 274·181), 195 (10), 192 (4), 153·091 (100, $C_9H_{13}O_2$ requires 153·093), 140 (12), 116 (34), 115 (10), 114 (99), 106 (6), 95 (9), 94 (11), 93 (12), 81 (17), 80 (55), 69 (13), 67 (12), 59 (10), 57 (11), 55 (18), 53 (17), 43 (28), 41 (30).

trans-4-(*Pyrrol-2-yl*)*but-3-en-2-one* (10).—2-Formylpyrrole (100 mg) and acetone (0·12 ml) were dissolved in water (2 ml), and potassium hydroxide solution (1N, 0·12 ml) was added. The mixture was kept at room temperature for 18 h and the precipitated crystals were filtered off and recrystallised twice from benzene to yield *trans*-4-(pyrrol-2-yl)but-3-en-2-one (80 mg) as lemon-yellow needles, m.p. 110°, $\lambda_{max.}$ (ethanol) 348 nm, $\nu_{max.}$ ($CHCl_3$) 3460, 1660, *1615*, *1595*, *1360*, 1130, 1120, 1090, and 960 cm^{-1}, δ ($CDCl_3$; 60 MHz), 2·33 (3H, s), 6·34 (1H, m), 6·62 (1H, m), 7·00 (1H, m), and 6·40 (1H, d, *J* 16 Hz), *m/e* 135 (100%; $M^{+\bullet}$), 134 (20), 120 (100), 106 (7), 93 (8), 92 (90), 91 (10), 80 (4), 79 (5), 78 (10), 77 (5), 66 (4), 65 (40), 64 (10), 63 (12), 52 (8), 51 (9), 43 (18), 41 (10),

39 (8) [lit.,[6] m.p. 112—114°, $\lambda_{max.}$ 353 (ε 23,000), $\nu_{max.}$ 1660, 1615, and 1594 cm^{-1}].

Methyl 3-(*Pyrrol*-2-*yl*)*prop*-2-*enoate* (1).—A solution of 2-formylpyrrole (50 mg) and methoxycarbonylmethylenetriphenylphosphorane (200 mg) in dry benzene (10 ml) was boiled under reflux for 1 h, cooled, and the benzene was removed under reduced pressure. Vacuum sublimation of the residual gum (70 and 0·1 mmHg) yielded *methyl* 3-(*pyrrol*-2-*yl*)*prop*-2-*enoate* (60 mg) as needles, m.p. 103°, $\lambda_{max.}$ (ethanol) 331 nm (ε 25,700) [the corresponding ethyl ester [6] has $\lambda_{max.}$ 331 nm (ε 25,800)], $\nu_{max.}$ ($CHCl_3$) 3460, 2980, 2940, 2840, 1690, 1630, 1545, 1130, 1120, 1090, and 970 cm^{-1}, δ ($CDCl_3$; 60 MHz) 3·78 (3H, s), 6·01 (1H, d, *J* 16 Hz), 6·25 (1H, m), 6·54 (1H, m), 6·90 (1H, m), 7·56 (1H, d, *J* 16 Hz), *m/e* 151 (100%, $M^{+\cdot}$), 120 (50), 119 (55), 93 (6), 92 (17), 91 (11), and 65 (8).

Methyl 2-*Methyl*-3-(*pyrrol*-2-*yl*)*prop*-2-*enoate* (2).—(a) 2-Formylpyrrole (20 mg) in dry benzene (1 ml) was added to a solution of α-methoxycarbonylethylidenetriphenylphosphorane (150 mg) in benzene (1 ml) and the mixture was boiled under reflux for 4 h. Removal of the solvent under reduced pressure yielded a gum which was purified by t.l.c. (silica gel HF 254, 12% acetone in benzene) and vacuum sublimation (70° and 0·1 mm Hg) to give *methyl* trans-2-*methyl*-3-(*pyrrol*-2-*yl*)*prop*-2-*enoate* (23 mg) as long needles, m.p. 100° (with sublimation), $\lambda_{max.}$ (ethanol) 325 nm (ε 25,500), $\nu_{max.}$ ($CHCl_3$) 3460, 2960, 2850, 1695, 1625, 1360, 1115, 1105, 910 cm^{-1}, δ ($CDCl_3$; 60 MHz) 2·18 (3H), 3·80 (3H, s), 6·35 (1H, m), 6·59 (1H, m), 6·95 (1H, m), 7·57br (1H), and 8·23br (1H), *m/e* 165 (100%; $M^{+\cdot}$), 134 (20), 133 (23), 106 (31), 105 (80), 104 (36), 79 (18), 77 (16), 53 (10), and 51 (10).

(b) α-Methoxycarbonylethyltriphenylphosphonium bromide (260 mg), 2-formylpyrrole (50 mg), and 1,2-epoxybutane (1 ml) were heated in a sealed tube at 100° for 20 min. The tube was cooled, broken open, and the contents were extracted into ether. The ethereal extracts were washed well with water, dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure to yield a gum which on t.l.c. (silica gel HF 254, 15% acetone in benzene) gave the *trans*-ester (31 mg), identical with the sample from (a), and the *cis*-ester (4 mg) as a yellow gum; $\lambda_{max.}$ (ethanol) 335 nm (ε 15,000), $\nu_{max.}$ (liquid film) 3390, 2950, 1690, 1605, 1530, 1360, 1250, 1220, 1090, and 1040 cm^{-1}, δ ($CDCl_3$; 60 MHz) 2·06 (3H, d, *J* 1·5 Hz), 3·79 (3H, s), 6·25 (1H, m), 6·42 (1H, m), 6·75br (1H), 6·94 (1H, m), 8·23br (1H).

Methyl 5-(*Pyrrol*-2-*yl*)*penta*-2,4-*dienoate* (3).—3-Methoxycarbonylprop-2-enylidenetriphenylphosphorane [11] (40 mg) was dissolved in dry benzene (1·5 ml) and 2-formylpyrrole (10 mg) was added. The solution was boiled under reflux for 1 h, cooled, and the benzene was removed under reduced pressure to yield a gum which was purified by column chromatography (silica gel, 10% acetone in benzene) and afforded *methyl* 5-(*pyrrol*-2-*yl*)*penta*-2,4-*dienoate* (12 mg) as yellow crystals, m.p. 130°, $\lambda_{max.}$ (ethanol) 368 nm (ε 34,500), $\nu_{max.}$ ($CHCl_3$) 3460, 2990, 2940, 1695, 1615, 1445, 1435, 1415, 1330, 1250, 1135, 1030, and 990 cm^{-1}, δ ($CDCl_3$; 100 MHz) 3·70 (3H, s), 6·22 (1H, m), 6·40 (1H, m), 6·82 (1H, m), 8·44br (1H), and 5·70—7·30 (4H, m), *m/e* 177 (40%, $M^{+\cdot}$), 147 (13), 146 (20), 118 (100), 117 (40), 91 (16), and 90 (10).

3-*Methoxycarbonyl*-1-*methylprop*-2-*enyltriphenylphosphonium Iodide*.—3-Methoxycarbonylprop-2-enylidenetriphenylphosphorane [11] (120 mg) was dissolved in dry benzene (1 ml) and the solution was added dropwise over 30 min to a refluxing solution of methyl iodide (1 g) in dry benzene (3 ml) and ethyl acetate (5 ml). The precipitated crystals of the phosphonium salt were filtered off, washed well with ethyl acetate, and dried at 0·1 mmHg for 4 h to give 3-*methoxycarbonyl*-1-*methylprop*-2-*enyltriphenylphosphonium iodide* (100 mg), m.p. 197—198°, $\lambda_{max.}$ (ethanol) 221 nm, $\nu_{max.}$ ($CHCl_3$) 1725, 1655, 1595, 1440, 1115, and 1000 cm^{-1}, δ ($CDCl_3$; 60 MHz) 3·68 (3H, s), 4·6—5·2 (m), 6·4—6·8 (m), 7·5—8·1 (*ca.* 15H, m) (Found: C, 57·15; H, 4·8; I, 25·55; P, 6·25. $C_{24}H_{24}IO_2P$ requires C, 57·4; H, 4·8; I, 25·25; P, 6·2%).

Treatment of 6-methoxycarbonylpenta-2,4-dienyltriphenylphosphonium bromide by the same procedure yielded a crystalline material, m.p. 175°, δ ($CDCl_3$; 60 MHz) 1·65—2·30 (2H, m), 3·70 (3H, m), 4·35—5·00 (m), and 7·50—8·00 (m), which was not the corresponding dienoate Wittig salt.

Methyl 4-*Methyl*-5-(*pyrrol*-2-*yl*)*penta*-2,4-*dienoate* (4a).—3-Methoxycarbonyl-1-methylprop-2-enyltriphenylphosphonium iodide (200 mg) was dissolved in water (20 ml) and dilute sodium hydroxide solution was added dropwise until the solution was alkaline to phenolphthalein paper. The resulting orange solution was extracted twice with benzene (30 ml) and the extracts were combined and dried ($MgSO_4$). The solution of the phosphorane was filtered and concentrated (to 3 ml) under reduced pressure. 2-Formylpyrrole (30 mg) was added and the solution was boiled under reflux for 1 h. Evaporation of the solvent gave a red gum which was purified by t.l.c. (silica gel, 17% acetone in benzene) to yield an oil which crystallised from ether to give *methyl* 4-*methyl*-5-(*pyrrol*-2-*yl*)*penta*-2,4-*dienoate* (45 mg) as needles, m.p. 114° (with sublimation), $\lambda_{max.}$ (ethanol) 368 nm (ε 34,000), $\nu_{max.}$ ($CHCl_3$) 3460, 2996, 2950, 2845, 1695, 1615, 1445, 1435, 1413, 1032, 990, 960, and 880 cm^{-1}, δ ($CDCl_3$; 100 MHz) 1·87 (3H, d, *J* 1·5 Hz), 3·73 (3H, s), 6·22 (1H, m), 6·38 (1H, m), 6·64 (1H, s), 6·82 (1H, m), and 7·32 (1H, dm, *J* 8·6 Hz), *m/e* 191 (44%, $M^{+\cdot}$), 160 (14), 146 (14), 132 (100), 131 (33), 130 (55), 118 (40), 104 (13), 95 (20), 91 (18), and 43 (45).

6-*Methoxycarbonylpenta*-2,4-*dienyltriphenylphosphonium Bromide*.—Triphenylphosphine (5·0 g) was dissolved in dry benzene (5 ml) and a solution of methyl 6-bromosorbate [13] (2·8 g) in benzene (1 ml) was added. The solution was heated under reflux for 1 h and then allowed to stand for a further 24 h. The precipitated phosphonium salt was filtered, washed with dry ether, and dried under vacuum to yield 6-*methoxycarbonylpenta*-2,4-*dienyltriphenylphosphonium bromide* (4·5 g), m.p. 188°, $\lambda_{max.}$ (ethanol) 265 and 220 nm, $\lambda_{max.}$ ($CHCl_3$) 261 nm, $\nu_{max.}$ ($CHCl_3$) 2930, 1705, 1640, 1615, 1590, 1440, 1110, and 995 cm^{-1}, $\nu_{max.}$ (Nujol) 1715, 1640, 1615, 1590, 1253, 1156, 1120, and 1005 cm^{-1}, δ ($CDCl_3$; 60 MHz) 3·68 (3H, s), 5·13 (2H, dd, J_1 16, J_2 7 Hz), 5·6—6·1 (m), 6·4—7·2 (m), 7·5—8·1 (*ca.* 15 H, m) (Found: C, 64·1; H, 5·2; P, 7·05. $C_{25}H_{24}BrO_2P$ requires C, 64·25; H, 5·2; P, 6·65%).

Methyl 7-(*Pyrrol*-2-*yl*)*hepta*-2,4,6-*trienoate* (5).—6-Methoxycarbonylpenta-2,4-dienyltriphenylphosphonium bromide (400 mg) was dissolved in water (20 ml) and sodium hydroxide solution (4N) was added until the solution was alkaline to phenolphthalein paper. Benzene was added and the phosphorane passed into the benzene layer. The organic layer was separated, dried ($MgSO_4$), and filtered. The solution was concentrated (to 1·5 ml) under reduced pressure and 2-formylpyrrole (30 mg) was added. The solution was boiled under reflux for 30 min, cooled, and the benzene was evaporated to leave a red gum, which was purified by t.l.c.

(silica gel, 20% acetone in benzene) to yield *methyl* 7-(*pyrrol*-2-*yl*)*hepta*-2,4,6-*trienoate* (39 mg) as yellow crystals, m.p. 160°, $\lambda_{max.}$ (ethanol) 394 nm (ε 43,000), $\nu_{max.}$ ($CHCl_3$) 3460, 2990, 2950, 1698, 1595, 1435, 1417, 1357, 1300, 1132, 1032, 995, and 882 cm^{-1}, δ ($CDCl_3$; 100 MHz) 3·70 (3H, s), 5·80 (1H, d, *J* 16 Hz), 5·80—7·50 (5H, m), 6·24 (1H, m), 6·36 (1H, m), 6·80 (1H, m), and 8·64br (1H), *m/e* 203 (34%, $M^{+\bullet}$), 172 (12), 170 (14), 144 (100), 117 (20), 115 (16), 104 (10), 91 (10), and 80 (12).

2-Methyl-3-(pyrrol-2-yl)prop-2-enal (9).—Formylethylidenetriphenylphosphorane (200 mg) and 2-formylpyrrole (40 mg) were intimately mixed and heated in a sealed tube for 40 min at 140°. The tube was cooled, broken open, and the contents were extracted into ether. T.l.c. of the mixture (silica gel HF 254, 17% acetone in benzene) yielded 2-*methyl*-3-(*pyrrol*-2-*yl*)*prop*-2-*enal* (65 mg) as pale yellow needles, m.p. 84°, $\lambda_{max.}$ (ethanol) 345 nm (ε 30,500), δ ($CDCl_3$; 60 MHz) 2·17 (3H), 6·38 (1H, m), 6·70 (1H, m), 7·12 (1H, m), 7·15br (1H), 8·40br (1H), and 9·45 (1H, s), *m/e* 135·069 (100%, $M^{+\bullet}$, C_8H_9NO requires 135·068), 107 (20), 106 (30), 104 (10), 80 (15), 79 (10), 77 (10), 67 (80), 51 (10), 41 (5), and 39 (10).

3-(*Pyrrol*-2-*yl*)*prop*-2-*enal* (8) (*with* E. A. Faruk).—2-Formylpyrrole (40 mg) and formylmethylenetriphenylphosphorane [14] (65 mg) in benzene (60 ml) were heated under reflux for 128 h. Removal of the solvent under reduced pressure followed by column chromatography (silica gel, 5% acetone in light petroleum) gave a red gum. T.l.c. (silica gel HF 254, 17% acetone in benzene) yielded trans-3-(*pyrrol*-2-*yl*)*prop*-2-*enal* (30 mg) as pale yellow crystals, m.p. 109—111°, $\lambda_{max.}$ (ethanol) 348 nm, $\nu_{max.}$ (Nujol) 3240, 2750, 1650, 1625, 1033, 1010, and 968 cm^{-1}, δ ($CDCl_3$; 60 MHz) 6·36 (2H, m and dd, J_1 15, J_2 8 Hz), 6·68 (1H, m), 7·03 (1H, m), 7·33 (1H, d, *J* 15 Hz), and 9·63 (1H, d, *J* 8 Hz), *m/e* 121 (100%, $M^{+\bullet}$), 120 (17), 93 (35), 92 (45), 91 (12), 80 (10), 67 (90), 65 (45), 63 (20), 52 (10), 51 (9), 50 (8), 41 (12), 40 (12), and 39 (61).

A second product from the reaction was 5-(*pyrrol*-2-*yl*)-*penta*-2,4-*dienal* which was recrystallised from ether–light petroleum as deep red crystals, m.p. 95—98°, $\lambda_{max.}$ (ethanol) 392 nm, $\nu_{max.}$ (Nujol) 3300, 2850, 2750, 1680, 1640, 1610, 1038, 1015, 989, and 969 cm^{-1}, δ ($CDCl_3$; 60 MHz) 6·0—7·4 (*ca.* 7H, m), and 9·56 (1H, d, *J* 8 Hz), *m/e* 147 (55%, $M^{+\bullet}$), 121 (63), 118 (100), 93 (64), 67 (78), 65 (59), and 39 (85). There were also products with $\lambda_{max.}$ (ethanol) 410 and 425 nm, probably the corresponding trienal and tetraenal, respectively.

5-*Methyl*-6-(*pyrrol*-2-*yl*)*hexa*-3,5-*dien*-2-*one* (13).—2-Methyl-3-pyrrol-2-ylprop-2-enal (5 mg) and acetone (0·1 ml) were dissolved in 50% aqueous methanol and dilute potassium hydroxide solution (4N, 0·1 ml) was added. The mixture was allowed to stand for 3 days and then extracted into ether. The extracts were washed with water, dried ($MgSO_4$), and filtered, and the filtrate was evaporated to yield a yellow solid. Recrystallisation from a mixture of ether and cyclohexane yielded 5-*methyl*-6-(*pyrrol*-2-*yl*)*hexa*-3,5-*dien*-2-*one* (6 mg) as lemon-yellow needles, m.p. 112°. $\lambda_{max.}$ (ethanol) 382 nm, δ ($CDCl_3$; 60 MHz) 2·10 (3H, d, *J* 1·3 Hz), 2·30 (3H, s), 6·32 (1H, m), 6·64 (1H, m), and 6·90 (1H, m), *m/e* 175·099 (80%, $M^{+\bullet}$, $C_{11}H_{13}NO$ requires 175·099), 160 (63), 132·081 (100, $C_9H_{10}N$ requires 132·081), 130 (22), 127 (70), 106·065 (10, C_7H_8N requires 106·065), 81 (21), and 43 (33).

Methyl 6-*Methyl*-7-(*pyrrol*-2-*yl*)*hepta*-2,4,6-*trienoate* (6).—3-Methoxycarbonylprop-2-enylidenetriphenylphosphorane (100 mg) and 2-methyl-3-(pyrrol-2-yl)prop-2-enal (15 mg) were dissolved in benzene and the solution was boiled under reflux for 3 h. Removal of the solvent under reduced pressure gave a yellow gum which was purified by t.l.c. (silica gel, 12% acetone in benzene) to yield a yellow solid. Recrystallisation of the solid from cyclohexane gave *methyl* 6-*methyl*-7-(*pyrrol*-2-*yl*)*hepta*-2,4,6-*trienoate* (10 mg) as yellow needles, m.p. 130°, $\lambda_{max.}$ (ethanol) 393 nm (ε 41,500), $\nu_{max.}$ ($CHCl_3$) 3460, 2995, 2940, 1698, 1595, 1435, 1418, 1135, 1032, 980, and 882 cm^{-1}, δ ($CDCl_3$; 100 MHz) 2·07 (3H), 3·72 (3H, s), 5·85 (1H, d, *J* 16 Hz), 6·00—7·50 (4H, m), 6·29 (1H, m), 6·32 (1H, m), 6·84 (1H, m), 8·26br (1H), *m/e* 217·100 (90%, $M^{+\bullet}$, $C_{13}H_{15}NO_2$ requires 217·100), 202 (24), 186 (18), 184 (38), 170 (20), 158·097 (100, $C_{11}H_{12}N$ requires 158·097), 157 (30), 156 (38), 143 (40), 131 (24), 104·050 (15, C_7H_6N requires 104·050), 91 (25), and 80 (30).

Methyl 8-*Methyl*-9-(*pyrrol*-2-*yl*)*nona*-2,4,6,8-*tetraenoate* (7).—6-Methoxycarbonylpenta-2,4-dienyltriphenylphosphonium bromide (200 mg) was dissolved in water (20 ml) and sodium hydroxide solution (4N) was added until the solution was alkaline to phenolphthalein paper. The liberated phosphorane was extracted into benzene and the organic layer separated, dried ($MgSO_4$), and filtered. The filtrate was concentrated (to 3 ml) under reduced pressure, and 2-methyl-3-(pyrrol-2-yl)prop-2-enal (17 mg) added. The solution was boiled under reflux for 1 h after which the benzene was evaporated to leave a red gum, which was purified by t.l.c. (silica gel, 17% acetone in benzene) and by recrystallisation from cyclohexane to yield *methyl* 8-*methyl*-9-(*pyrrol*-2-*yl*)*nona*-2,4,6,8-*tetraenoate* (20 mg) as fine orange needles, m.p. 171°, $\lambda_{max.}$ (ethanol) 409 nm (ε 43,200), $\nu_{max.}$ ($CHCl_3$) 3460, 2990, 2945, 1695, 1593, 1433, 1419, 1132, 1033, 980, and 882 cm^{-1}, δ ($CDCl_3$; 100 MHz) 2·10 (3H), 5·80 (1H, d, *J* 16 Hz), 6·24 (1H, m), 6·25—7·40 (6H, m), 6·36 (1H, m), 6·80 (1H, m), and 8·19br (1H), *m/e* 243·127 (100%, $M^{+\bullet}$, $C_{15}H_{17}NO_2$ requires 243·126), 184·113 (55, $C_{13}H_{14}N$ requires 184·113), 168 (30), 144 (50), 106·066 (20, C_7H_8N requires 106·066), 91 (40), 84 (43), 80 (35), 67 (60), 55 (58), and 41 (50).

Methyl 4-*Methyl*-5-(*pyrrol*-2-*yl*)*penta*-2,4-*dienoate* (4b).—2-Methyl-3-(pyrrol-2-yl)prop-2-enal (10 mg) and methoxycarbonylmethylenetriphenylphosphorane (100 mg) were dissolved in dry benzene (1 ml) and the solution was boiled under reflux for 6 h. Evaporation of the benzene gave a yellow oil which was purified by t.l.c. (silica gel, 12% acetone in benzene) to give a yellow solid. Recrystallisation from cyclohexane yielded *methyl* 4-*methyl*-5-(*pyrrol*-2-*yl*)-*penta*-2,4-*dienoate* (12 mg) as yellow needles, m.p. 123°, $\lambda_{max.}$ (ethanol) 364 nm (ε 34,000), $\nu_{max.}$ ($CHCl_3$) 3460, 2995, 2850, 1695, 1445, 1433, 1415, 1032, 985, and 882 cm^{-1}, δ ($CDCl_3$; 100 MHz) 2·07 (3H), 3·74 (3H, s), 5·86 (1H, d, *J* 16 Hz), 6·28 (1H, m), 6·44 (1H, m), 6·57 (1H, s), 6·86 (1H, m), and 7·42 (1H, d, *J* 16 Hz), *m/e* 191·094 (45%, $M^{+\bullet}$, $C_{11}H_{13}NO_2$ requires 191·095), and 132·081 (100, $C_9H_{10}N$ requires 132·081).

Methyl 8-*Methyl*-9-(*pyrrolidin*-2-*yl*)*nonanoate*.—Methyl 8-methyl-9-(pyrrol-2-yl)nona-2,4,6,8-tetraenoate (7) (3 mg) was dissolved in ethanol (0·5 ml) and the solution added to a previously hydrogenated suspension of Adams catalyst (10 mg) in ethanol (0·5 ml). The resulting suspension was stirred and hydrogenated at room temperature and atmospheric pressure for three days. Filtration of the solution and removal of the ethanol yielded a gum which was purified by t.l.c. (silica gel, 10% ethanol in benzene containing 2% v/v concentrated aqueous ammonia) to give *methyl* 8-*methyl*-9-(*pyrrolidin*-2-*yl*)*nonanoate* (2 mg) as an oil

which showed only end absorption in the u.v. spectrum, *m/e* 255·220 (20%, $M^{+\bullet}$, $C_{15}H_{19}NO_2$ requires 255·220), 254 (16), 240 (10), 224 (20), 151 (25), 149 (25), 112·113 (22, $C_7H_{14}N$ requires 112·113), 98 (40), 80 (45), 74 (30), 70 (100), 59 (10), 55 (20), and 43 (50).

General Method for the Reduction of the Model Carboxylic Esters to the Corresponding Alcohols.—The ester (4 mg) was dissolved in ether (1 ml) and the solution cooled in ice. To the solution an ice cold suspension of lithium aluminium hydride (10 mg) in ether (1 ml) was added dropwise over 5 min. The solution was kept at 0° for a further 5 min, and sodium potassium tartrate solution was added cautiously with cooling until the excess of lithium aluminium hydride had been destroyed. The suspension was extracted with ether and the layer was separated, dried ($MgSO_4$), and filtered. Evaporation of the filtrate to dryness under a stream of nitrogen yielded the alcohol (*ca.* 3 mg). The u.v. absorption maxima of the alcohols (in benzene) are recorded in Table 2.

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