144. *Chemistry of the Higher Fungi. Part X.* Further Polyacetylenic Derivatives of Decane from Various Basidiomycetes.*

By J. N. Gardner, E. R. H. Jones, P. R. Leeming, and J. S. Stephenson.

The isolation and characterisation of several polyacetylenic derivatives of decane from species of five genera of Basidiomycetes are described. Six of the compounds have not hitherto been recognised as fungal metabolites.

Polyacetylenic compounds have been isolated from diverse plant types, cultures of the higher fungi having been a particularly fruitful source.[1] Compounds varying in chain length from C_8 to C_{12} have been isolated from Basidiomycetes, and an Actinomycete (*Nocardia acidophilus*) produces the one example of a C_{13} compound, *viz.*, mycomycin.[2] It is desirable fully to explore the range of polyacetylene types produced by the higher fungi so as to determine the structural pattern which should throw light on the biogenesis of this novel group of natural products. Preliminary work along these lines was indicated in Part VIII.[3] A more detailed examination of many species of Basidiomycetes obtained

* Part IX, *J.*, 1959, 2197.

[1] Bohlmann and Mannhardt, *Fortschr. Chem. org. Naturstoffe*, 1957, **14**, 1; Bu'Lock, *Quart. Rev.*, 1956, **10**, 371; Wailes, *Rev. Pure Appl. Chem.* (*Australia*), 1956, **6**, 61.

[2] Celmer and Solomons, *J. Amer. Chem. Soc.*, 1952, **74**, 1870, and subsequent papers.

[3] Bu'Lock, Jones, and Turner, *J.*, 1957, 1607.

from the Forest Products Research Laboratory and the Type Culture Collection, Baarn (Netherlands), is now being undertaken. A systematic screening (details of the technique are given in the Experimental section) of some 300 Basidiomycetes belonging to the class Hymenomycetes, has indicated that approximately 10% produce polyacetylenes, *i.e.*, extracts show appreciable ultraviolet absorption with some polyacetylenic fine structure. In this way it is possible to detect in extracts the presence of compounds containing as minimum unsaturation the enediyne (C=C–C≡C–C≡C) chromophore; more saturated systems, *e.g.*, diacetylenic and vinylacetylenic, would escape notice. The culture fluid extracts were separated into an acidic and a neutral fraction: the former was methylated and the two fractions were separately chromatographed on alumina. In no case could any significant amount of polyacetylenic material be extracted from the mycelia (cf. *P. anthracophilus* [3]).

It soon became clear that many of the " positive " fungi produced compounds identical with or closely related to those already isolated from cultures of *Polyporus anthracophilus*,[3] *i.e.*, derivatives of decane varying in the extent of unsaturation and degree of oxidation at either end of the chain. Such products have been obtained from five fungi; *Merulius lacrymans* yielded compounds (I and II; R = H); *Polyporus guttulatus* (III; R = H) and (IV); *Pleurotus ulmarius* (VI and VII; R = H), (VIII) and (IX); *Tricholoma panaeolum* (III and VII; R = H); and *Leptoporus kymantodes* gave (IV) (stereochemistry not determined in this case). It appears that C_{10} polyacetylenic compounds are fairly widely distributed among the Basidiomycetes; Sörensen [4] has shown that the related matricaria ester (V) is present in species belonging to 6 of the 13 tribes of the Compositæ family.

Merulius lacrymans (dry rot fungus). The methylated acidic fraction yielded compounds (I) and (II) (R = Me). The major component (*ca.* 30 mg. per litre of culture fluid), the diester (I), had ultraviolet absorption characteristic of the triyne-carbonyl chromophore, and infrared absorption in the carbonyl region typical of both saturated and conjugated ester groupings. Since hydrogenation and subsequent hydrolysis yielded sebacic acid, the structure (I) is unambiguously established. Hydrolysis yielded the diacid (I; R = H) identical with material obtained (silica-gel chromatography) from the crude acidic extracts of the culture fluid, thus proving that it is the dicarboxylic acid and not a half-ester that occurs naturally. The minor component was identified as the diester of the acid (II; R = H), previously isolated from *P. anthracophilus* and also synthesised.[3]

Polyporus guttulatus. By chromatography of the methylated acid fraction the diester (III; R = Me) was obtained. The neutral fraction yielded a low-melting alcohol, characterised as its *p*-phenylazobenzoate. The alcohol had ultraviolet absorption typical of the enediynene chromophore, but a small amount (<5%) of enediyne type of absorption was also observed. Neither chromatography nor crystallisation removed this contaminant and it persisted in the *p*-phenylazobenzoate even after repeated crystallisation. The infrared absorption spectrum of the alcohol showed bands attributable to both *cis*- and *trans*-ethylenic hydrogen and a C–O stretching mode at 1022 $cm.^{-1}$. This is probably associated with a hydroxyl group allylic to a *cis*-disubstituted double bond; a hydroxyl group allylic to a *trans*-double bond shows [5] two bands (1090 and 1030 $cm.^{-1}$). Since hydrogenation gave decanol the alcohol had to be the deca-*cis*-2,*trans*-8-diene-4,6-diyn-1-ol (IV); coupling [6] of *trans*-1-bromopent-3-en-1-yne and *cis*-pent-2-en-4-yn-1-ol afforded (IV), identical in all respects to the natural alcohol.

Pleurotus ulmarius. Chromatography of the methylated acids yielded two compounds, the less polar being *trans*-dehydromatricaria ester (VI; R = Me). The other had ultraviolet absorption typical of the carbonyl-enetriyne chromophore, and the infrared absorption spectrum showed the presence of conjugated-ester and hydroxyl groupings.

[4] Sörensen and Stene, *Annalen*, 1941, **549**, 80; Holme and Sörensen, *Acta. Chem. Scand.*, 1954, **8**, 34.
[5] Unpublished observations from this laboratory.
[6] Chodkiewicz, *Ann. Chim.* (*France*), 1957, **2**, 819.

Hydrogenation, oxidation, and hydrolysis yielded sebacic acid thus establishing the structure as (VII; R = Me), the ω-hydroxylated analogue of the less-polar constituent. Coupling [6] of *trans*-5-bromopent-2-en-4-yn-1-oic acid and penta-2,4-diyn-1-ol, followed by methylation of the product afforded ester (VII; R = Me), identical in all respects with the ester of the natural acid.

Chromatography of the neutral fraction yielded an aldehyde and an alcohol. The latter was identified as *trans*-dec-2-ene-4,6,8-triyn-1-ol (IX), already synthesised by

(I)	$RO_2C\cdot CH_2\cdot CH_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot C{\equiv}C\cdot CO_2R$	(1)
(II)	$RO_2C\cdot CH_2\cdot CH_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{t}{C}H{=}CH\cdot CO_2R$	(2)
(III)	$RO_2C\cdot \overset{t}{C}H{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{t}{C}H{=}CH\cdot CO_2R$	(2)
(IV)	$CH_3\cdot \overset{t}{C}H{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{c}{C}H{=}CH\cdot CH_2\cdot OH$	(1, 4)
(V)	$CH_3\cdot \overset{c}{C}H{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{c}{C}H{=}CH\cdot CO_2Me$	(3)
(VI)	$CH_3\cdot C{\equiv}C\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{t}{C}H{=}CH\cdot CO_2R$	(3)
(VII)	$HO\cdot CH_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{t}{C}H{=}CH\cdot CO_2R$	(1, 4)
(VIII)	$CH_3\cdot C{\equiv}C\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{t}{C}H{=}CH\cdot CHO$	(1, 4)
(IX)	$CH_3\cdot C{\equiv}C\cdot C{\equiv}C\cdot C{\equiv}C\cdot \overset{t}{C}H{=}CH\cdot CH_2\cdot OH$	(3, 4)

1. New compounds. 2. Also produced by *P. anthracophilus*.[3] 3. Previously synthesised. 4 Syntheses described in this paper.

Chodkiewicz.[6] The infrared absorption spectrum of the aldehyde showed a band at 1111 cm.$^{-1}$ which has been found to be associated with the C–CHO stretching mode of the *trans*-C≡C–CH=CH–CHO grouping.[5] Since reduction with sodium borohydride gave the alcohol (IX) the aldehyde must be (VIII); this was confirmed by its preparation from (IX) by oxidation with manganese dioxide.

Tricholoma panaeolum. The methylated acidic fraction yielded the hydroxy-ester (VII; R = Me) as the major constituent, albeit only in very small amount (*ca.* 1 mg. per litre), together with a trace of (III; R = Me).

Leptoporus kymantodes. The neutral fraction from this fungus exhibited enediynene absorption. Alumina chromatography gave a crude concentrate; its polarity was that of a monoalcohol, and hydrogenation gave decanol. The structure of the major polyacetylenic product from this fungus is therefore (IV) but the small amount available did not allow any stereochemical assignments to be made.

Since a considerable number of C_{10} fungal polyacetylenes with a range of unsaturation and oxygen functions are now known, any more detailed studies of fungi producing such compounds are not at present desirable. The above method of chain-length determination (including lithium aluminium hydride reduction of acids and aldehydes) has therefore been adopted as part of the standard preliminary investigation for all fungi producing polyacetylenes containing only one functional group. In this way *Polyporus floriformis* was shown to produce C_{10} derivatives and these were not further examined.

The compounds isolated from the above fungi provide further illustration of the structural pattern originally revealed by the many polyacetylenes produced by *P. anthracophilus*. Constituents with terminal methyl groups, presumably formed from five acetate units (cf. Bu'Lock and Gregory [7]), are accompanied by products (alcohols and acids) of their ω-oxidation. None of these fungi possesses enzyme systems capable of effecting the carbon–carbon bond fission believed [7,8] to be responsible for the formation of the polyacetylenes containing an odd number of carbon atoms.

[7] Bu'Lock and Gregory, *Biochem. J.*, 1959, **72**, 322.
[8] Jones and Stephenson, *J.*, 1959, 2197.

Experimental

Ultraviolet (Cary double-beam recording spectrophotometer) and infrared absorption spectra were recorded in ethanol and carbon disulphide respectively except where otherwise stated. M. p.s (corrected) were determined on a Kofler block. Alumina for chromatography was Peter Spence grade " H," deactivated by treatment with 5% of 10% acetic acid. Light petroleum refers to the fraction with b. p. 60—80°. Evaporations were carried out under reduced pressure. Vapour-phase chromatography was done on a column of 5% polyethylene glycol and 2% stearic acid supported on firebrick (50—90 mesh) with hydrogen as carrier gas at a flow rate of 60 c.c./min., a flame ionisation detector being used. The column measured 102 × 0·45 cm. and was kept at 120°.

Screening of Fungi.—Slope cultures of the fungi are grown on 3% malt agar and plated on to a similar medium, providing inoculum for two surface culture flasks one containing 3% malt solution (750 c.c.) and the other corn-steep medium (750 c.c.). The mycelial mat is supported on glass wool. 30 Days after inoculation the culture fluid from the flask showing the better growth is extracted with ether (1 × 100 and 2 × 50 c.c.), and the combined extracts are examined spectrographically. A portion of mycelium is cut up and extracted with alcohol and this extract is also examined. The second flask is sampled similarly after 80 days. The fungi whose extracts show ultraviolet absorption spectra typical of polyacetylenes (*i.e.*, the " positive " fungi) are then grown on a larger scale, generally 30 flasks. The production of poly-ynes is followed by weekly withdrawals (20 c.c.) of culture medium from any two flasks. The samples are extracted with ether and the extracts assayed for poly-yne content by measurement of the intensity of the longest wavelength absorption band in the ultraviolet region. When the concentration of poly-yne reaches a maximum, the culture fluid is poured off and continuously extracted with ether. The mycelial mats are reflooded with 4% glucose and 0·2M-sodium acetate and the polyacetylene production followed as above. Generally only one reflooding is worthwhile.

Merulius lacrymans.—The fungus was grown on corn-steep liquor. The concentration of polyacetylenes was maximal 50 days after inoculation. The culture fluid (4·5 l.) was then continuously extracted with ether (60 hr.) and the extract divided into an acidic and a neutral fraction with sodium hydrogen carbonate solution. The neutral portion showed no polyacetylene absorption and was discarded. The acidic fraction, containing approximately 140 mg. of polyacetylenes, was esterified with 3% sulphuric acid in methanol, and the product adsorbed from light petroleum (8 c.c.) on to alumina (8 g.). Light petroleum (80 c.c.) eluted the diester (I; R = Me), and petroleum–benzene (2 : 1) eluted small quantities of (II; R = Me). The ratio of the two compounds was *ca.* 100 : 1.

The crude acids (300 mg.) from another batch were chromatographed in ether on silica gel (550 c.c.). The diacid (II; R = H) was eluted first, followed by the diacid (I; R = H). Repeated chromatography of the latter and precipitation from ether with benzene yielded the diacid (I; R = H) as a pale yellow solid whose infrared absorption spectrum was identical with that of deca-2,4,6-triyne-1,10-dioic acid (see below).

Dimethyl deca-2,4,6-triyne-1,10-dioate (I; R = Me). Rechromatography of the crude ester (I; R = Me) on alumina and crystallisation from hexane at −70° afforded the *ester* as needles (43 mg.), m. p. 45—45·5° (Found: C, 66·4; H, 4·4. $C_{12}H_{10}O_4$ requires C, 66·05; H, 4·6%); $\lambda_{max.}$ 3290 (ε 3080), 3070 (ε 4800), 2880 (ε 3940), 2720 (ε 2370), 2570 (ε 1150), 2260 (ε 102,000), 2170 (ε 83,900), 2090 Å infl. (ε 53,800); $\nu_{max.}$ (in carbon tetrachloride) 1745 and 1721 cm.$^{-1}$ (unconjugated and conjugated ester carbonyl). The compound (16 mg.), hydrogenated in hexane over Adams platinum catalyst (22 mg.), took up 5·7 mol. of hydrogen. Alkaline hydrolysis of the product gave sebacic acid (9 mg.) which after two crystallisations from ethyl acetate had m. p. 131—134° and mixed m. p. 131—133° with authentic material.

Deca-2,4,6-triyne-1,10-dioic acid (I; R = H). The diester (I; R = Me) (73 mg.) in dioxan (32 c.c.) was added to potassium hydroxide (62 mg.) in water (8 c.c.), and the mixture kept at 20° under nitrogen for 24 hr. The acidic product (58 mg.) was isolated and fractionally precipitated from acetone–hexane to give the *acid* as an amorphous powder, decomp. 170° (Found: C, 63·1; H, 3·2. $C_{10}H_6O_4$ requires C, 63·2; H, 3·2%); $\lambda_{max.}$ 3270 (ε 2410), 3060 (ε 3900), 2870 (ε 3340), 2715 (ε 2150), 2570 (ε 1410), 2440 infl. (ε 1090), 2225 (ε 141,000), 2140 Å (ε 122,000); $\nu_{max.}$ (Nujol) 1690 cm.$^{-1}$ broad (unconjugated and conjugated carboxyl).

Dimethyl trans-*dec-2-ene-4,6-diyne-1,10-dioate* (II; R = Me). Rechromatography of accumulated material on alumina and crystallisation from hexane at −70° yielded (II; R = Me)

as needles (0·8 mg.), m. p. 50—55°. The infrared spectrum was practically identical with that of a specimen, m. p. 56·5—58°, from *P. anthracophilus*.[3]

Polyporus guttalatus.—The fungus was grown on malt medium for 56 days. The culture fluid (21 l.) was continuously extracted with ether, and the extract divided into an acidic and a neutral fraction.

Dimethyl deca-trans-2,trans-8-*diene*-4,6-*diyne*-1,10-*dioate* (III; R = Me). The acidic fraction was methylated in the usual way and purified by chromatography on alumina. Light petroleum–benzene (1 : 1) eluted the diester (20 mg.) which crystallised from hexane as plates, m. p. 103—106°, identical in all respects to the material obtained by Bu'Lock, Jones, and Turner.[3]

Deca-cis-2,trans-8-*diene*-4,6-*diyn*-1-*ol* (IV). The neutral fraction from 60 l. of culture medium was adsorbed from light petroleum (20 c.c.) on to alumina (25 g.). Benzene (60 c.c.) eluted material which, after two crystallisations from hexane at −70°, gave the alcohol (IV) as needles (20 mg.), m. p. below 20° (see below); $\lambda_{max.}$ 3125 (ε 17,500), 2935 (ε 21,100), 2765 (ε 14,200), 2615 (ε 7400), 2465 (ε 20,600), 2375 (ε 28,400), 2300 (ε 28,400), 2135 Å (ε 28,000) (this reveals the presence of *ca.* 5% of enediyne as a contaminant); $\nu_{max.}$ 3570 (hydroxyl), 1022 (C–O stretching), 944, and 730 cm.$^{-1}$ (*trans*- and *cis*-ethylenic hydrogen, respectively). The alcohol gave in good yield a *p*-phenylazobenzoate which crystallised from ethanol as orange laths, m. p. 140—142° (see below); $\lambda_{max.}$ 3140 (ε 40,000), 2945 (ε 33,200), 2775 (ε 20,600), 2640 (ε 12,000), 2300 (ε 38,900), 2140 Å (ε 34,800). Hydrogenation of the crude alcohol (12 mg.) containing *ca.* 10% of enediyne with 5% palladium on charcoal (20 mg.) gave decanol, identified by vapour-phase chromatography and by its *p*-phenylazobenzoate, m. p. 58·5—59·5° undepressed on admixture with an authentic sample.

trans-1-Bromopent-3-en-1-yne (120 mg.) in methanol (1 c.c.) was added during 5 min. under nitrogen to a stirred solution of *cis*-pent-2-en-4-yn-1-ol (60 mg.) and cuprous chloride (5 mg.) in aqueous ethylamine (2 c.c.; 30%) kept at 35°. During the addition, hydroxylamine hydrochloride was added to keep the copper reduced. Potassium cyanide (50 mg.) and water were then added and the mixture was extracted with ether. The ethereal solution was washed with water and dried, and the solvent removed. The residue was adsorbed from light petroleum (20 c.c.) on to alumina (100 g.). Elution with the same solvent (200 c.c.) afforded a hydrocarbon containing the enediynene chromophore (10 mg.; estimated spectroscopically). Ether–benzene (5 : 95; 200 c.c.) eluted the *alcohol* (IV; 90 mg.) which crystallised from hexane at −40°; it had m. p. 15—16° (Found: C, 82·1; H, 7·5. $C_{10}H_{10}O$ requires C, 82·2; H, 6·9%); $\lambda_{max.}$ 3125 (ε 18,200), 2935 (ε 22,200), 2765 (ε 14,000), 2615 (ε 7300), 2460 (ε 20,900), 2370 (ε 29,800), 2295 (ε 30,000), and 2165 Å (ε 28,200); $\nu_{max.}$ identical with that of natural material. The p-*phenylazobenzoate* had m. p. 144—145° (Found: C, 78·6; H, 5·2; N, 7·3. $C_{23}H_{18}O_2N_2$ requires C, 77·95; H, 5·1; N, 7·9%); $\lambda_{max.}$ 3140 (ε 43,000), 2950 (ε 37,000), 2780 (ε 20,800), 2625 (ε 12,000), 2450 (sh.), 2350 (sh.), 2300 (ε 44,000) and 2170 Å (sh.).

Pleurotus ulmarius.—During initial growth on malt for 31 days, the fungus produced, as judged from ultraviolet absorption spectra of extracts, mainly the acid (VII; R = H) and the alcohol (IX). Reflooding with glucose–acetate medium produced, after 16 days, proportionately less acid (VII; R = H) but the aldehyde (VIII) appeared. A second reflooding and growth for a further 15 days gave only the aldehyde (VIII) and alcohol (IX). A third reflooding was unsuccessful. The combined culture media from these experiments (3 × 15 l.) were extracted continuously with ether for 48 hr., and the extract divided into an acid and a neutral fraction.

Acid fraction. This was esterified with 3% sulphuric acid in methanol for 4 days at 20° and the product adsorbed on alumina (10 g.) from benzene–light petroleum (5 : 3). Elution with this solvent (40 c.c.) gave the ester (VI; R = Me), and benzene (200 c.c.) eluted the hydroxy-ester (VII; R = Me).

Methyl trans-*dec*-2-*ene*-4,6,8-*triynoate* (VI; R = Me). Rechromatography of this compound on alumina and crystallisation from hexane at −70° afforded the ester (0·8 mg.), m. p. 105—106° (cf. m. p. 105·5° recorded by Sörensen *et al.*[9]); $\lambda_{max.}$ (hexane) 3440 (ε 30,500), 3200 (ε 39,900), 3010 (ε 25,800), 2830 (ε 11,300), 2675 (ε 6260), 2560 (ε 84,100), 2440 (ε 52,800), 2325 infl. (ε 17,700), 2185 Å infl. (ε 16,800); $\nu_{max.}$ 1725 (conjugated ester), 950 cm.$^{-1}$ (*trans*-ethylenic hydrogen).

Methyl trans-10-*hydroxydec*-2-*ene*-4,6,8-*triyn*-1-*oate* (VII; R = Me). Evaporation of the

[9] Sörensen, Bruun, Holme, and Sörensen, *Acta Chem. Scand.*, 1954, **8**, 26.

fractions containing this compound gave a pale yellow solid (28 mg.). Two crystallisations from methylene chloride–hexane yielded the *ester* (8·5 mg.) as needles, decomp. *ca.* 115° (Found: C, 70·3; H, 4·5. $C_{11}H_8O_3$ requires C, 70·2; H, 4·3%); $\lambda_{max.}$ 3435 (ε 18,200), 3205 (ε 24,200), 3010 (ε 16,500), 2830 (ε 8260), 2565 (ε 73,000), 2450 Å (ε 53,800); $\nu_{max.}$ (in carbon tetrachloride) 3600 (hydroxyl), 1730 (conjugated ester), 953 cm.$^{-1}$ (*trans*-ethylenic hydrogen). The ester (23 mg.) was hydrogenated in ethanol over 5% palladium on charcoal (42 mg.) and took up 6·9 mol. of hydrogen. The product was oxidised with an excess of 8N-chromic acid in acetone (5 c.c.). Hydrolysis of the product and two crystallisations from ethyl acetate gave sebacic acid (6 mg.), m. p. and mixed m. p. 131—133°.

trans-5-*Bromopent*-2-*en*-4-*yn*-1-*oic acid*. A solution of *trans*-pent-2-en-4-yn-1-oic acid (0·95 g.) in 2N-sodium hydroxide (5 c.c.) was cooled to 0° and sodium hypobromite solution [9 c.c. of a mixture of ice (50 g.), 10N-sodium hydroxide (25 c.c.), bromine (5·5 c.c.), and water (10 c.c.)] added during 15 min. The mixture was stirred for 10 min. and then acidified with hydrochloric acid. Crystallisation of the precipitate (1·43 g., 83%) from hexane gave trans-5-*bromopent*-2-*en*-4-*yn*-1-*oic acid* as plates, m. p. 137—138° (decomp.) (Found: C, 34·6; H, 1·8; Br, 45·35. $C_5H_3O_2Br$ requires C, 34·3; H, 1·7; Br, 45·7%).

Synthesis of Methyl trans-10-*Hydroxydec*-2-*ene*-4,6,8-*triyn*-1-*oate* (VII; R = Me).—To a stirred solution of cuprous chloride (1 mg.) in aqueous ethylamine (33%; 1 c.c.) was added penta-2,4-diyn-1-ol (84 mg.) in methanol (0·5 c.c.). To this mixture in nitrogen at 40°, *trans*-5-bromopent-2-en-4-yn-1-oic acid (175 mg.) in methanol (0·4 c.c.) was added during 10 min. Crystals of hydroxylamine hydrochloride were added as required to reduce any cupric ion formed. After treatment with potassium cyanide (10 mg.) and water, the mixture was acidified and extracted with ether. The extract was methylated with diazomethane (from 300 mg. of methylnitrosourea). The solution was washed (sodium hydrogen carbonate solution) and evaporated to yield a yellow solid (175 mg.) which was adsorbed on to alumina from benzene. Elution with benzene gave a little of the diester (III; R = Me), from self-coupling of the bromoacetylene, and then the desired hydroxy-ester (VII; R = Me; 70% estimated spectroscopically). Crystallisation from methylene chloride–hexane gave a product identical in all respects with the naturally derived ester.

Neutral Fraction from Pleurotus ulmarius.—Chromatography on alumina (60 g.) and elution with benzene gave first the aldehyde (VIII) and then the alcohol (IX).

trans-*Dec*-2-*ene*-4,6,8-*triyn*-1-*ol* (IX). Evaporation of the chromatogram fractions gave a solid which, when crystallised from methylene chloride–hexane, gave the alcohol (88 mg.) as needles, m. p. 128—129° (decomp.) (Chodkiewicz [6] gives m. p. 129°) (Found: C, 83·3; H, 5·6. Calc. for $C_{10}H_8O$: C, 83·3; H, 5·6%); $\lambda_{max.}$ 3285 (ε 13,000), 3070 (ε 19,100), 2885 (ε 14,400), 2720 (ε 7580), 2570 (ε 3730), 2415 (ε 138,000), 2300 (ε 82,600), 2210 (infl.) (ε 37,300), 2100 Å (ε 44,100); $\nu_{max.}$ 3600 (hydroxyl), 950 (sh.), and 940 cm.$^{-1}$ (*trans*-ethylenic hydrogen). The product was identical in all respects with synthetic material.

trans-*Dec*-2-*ene*-4,6,8-*triyn*-1-*al* (VIII).—(*a*) The early chromatographic fractions were rechromatographed in light petroleum and then crystallised from hexane to give the *aldehyde* as pale yellow needles (21 mg.), m. p. 108—109° (decomp.) (Found: C, 84·3; H, 4·3. $C_{10}H_6O$ requires C, 84·5; H, 4·3%); $\lambda_{max.}$ (in hexane) 3500 (ε 36,500), 3260 (ε 44,400), 3060 (ε 27,800), 2880 (ε 11,900), 2720 infl. (ε 7290), 2580 (ε 86,900), 2455 (ε 49,100), 2345 infl. (ε 21,200), 2250 Å infl. (ε 20,600); $\nu_{max.}$ 1693 (conjugated aldehyde), 1111 (C–CHO stretching), 950 cm.$^{-1}$ (*trans*-ethylenic hydrogen). Treatment of the aldehyde (2·5 mg.) with an excess of potassium borohydride in methanol (5 c.c.) gave the alcohol (IX; 1·4 mg.) which, after chromatography and crystallisation, was identical with the natural material.

(*b*) *Synthesis*. Synthetic alcohol (IX) (59 mg.) was shaken with active manganese dioxide (500 mg.) [10] in methylene chloride (25 c.c.) for 18 hr. Isolation in the usual manner and crystallisation from hexane gave the aldehyde (23 mg., 40%), m. p. 108—109° (decomp.). It was identical in all respects with the natural material.

Tricholoma panaeolum.—The fungus was grown on malt medium for 24 days. The culture fluid (15 l.) was continuously extracted with ether, and the extract divided into an acidic and a neutral fraction, the latter being discarded. Methylation of the acidic fraction and chromatography on alumina afforded the diester (III; R = Me; 1 mg.) and hydroxy-ester (VII; R = Me; 18 mg.). Each compound was identical in all respects with the compounds isolated from *Polyporus guttulatus* and *Pleurotus ulmarius*, respectively.

[10] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

Leptoporus kymantodes.—The fungus was grown on malt medium for 28 days. The culture fluid (3 l.) was extracted in the usual way and the neutral portion of the extract was chromatographed. Ether–benzene (1 : 9) eluted an alcohol fraction (30 mg.); $\lambda_{max.}$ (ether) 3115, 2920, 2760, and 2600 Å. Hydrogenation over platinum gave decanol, identified by vapour-phase chromatography.

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