Pigments of Higher Fungi: A Review

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Abstract

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This review surveys the literature dealing with the structure of pigments produced by fungi of the phylum Basidiomycota and also covers their significant colourless precursors that are arranged according to their biochemical origin to the shikimate, polyketide and terpenoid derived compounds. The main groups of pigments and their leucoforms include simple benzoquinones, terphenylquinones, pulvinic acids, and derived products, anthraquinones, terpenoid quinones, benzotropolones, compounds of fatty acid origin and nitrogen-containing pigments (betalains and other alkaloids). Out of three orders proposed, the concern is only focused on the orders Agaricales and Boletales and the taxonomic groups (*incertae sedis*) Cantharellales, Hymenochaetales, Polyporales, Russulales, and Telephorales that cover most of the so called higher fungi often referred to as mushrooms. Included are only the European species that have generated scientific interest due to their attractive colours, taxonomic importance and distinct biological activity.

Keywords: higher fungi; Basidiomycota; mushroom pigments; mushroom colour; pigment precursors

Mushrooms inspired the cuisines of many cultures (notably Chinese, Japanese and European) for centuries and many species were used in folk medicine for thousands of years. However, little is known that mushrooms were a commonly used textile dye before the invention of synthetic dyes because of the vast range of vivid and rich colours achievable (Mussak & Bechtold 2009). The chromophores of mushroom dyes contain a variety of fascinating organic compounds. Their pigmentation may vary with the age and some undergo distinctive colour changes on bruising; therefore, the colours of mushrooms are one of the essential features used in their identification. Furthermore, the pigments of mushrooms may protect the organism from UV damage and bacterial attack or play a role as insect attractants.

Mushrooms do not contain the pigments that dominate in higher plant colours. Chlorophylls and anthocyanins are not present in fungi at all; betalains, carotenoids and other terpenoids are widespread only in some species of higher fungi. Many of the pigments of higher fungi are quinones or similar conjugated structures that are mostly classified according to the perceived biosynthetic pathways, reflecting their structure, to pigments derived from (*i*) the shikimate (chorismate) pathway, (*ii*) the acetate-malonate (polyketide) pathway, (*iii*) the mevalonate (terpenoid) pathway, and (*iv*) pigments containing nitrogen. Several review articles covering the literature published from its inception during the latter half of the 19th century to the end of 2009 have been already published (Gill & Steglich 1987; Gill 1994, 1996, 1999, 2003; Hanson 2008a,b; Räisänen 2009; Zhou & Liu 2010).

The shikimate pathway provides a route to the essential amino acids phenylalanine, tyrosine and tryptophan via the central intermediates shikimic and chorismic acids. Phenylalanine and tyrosine are precursors for a wide range of compounds includ-

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ing arylpyruvic, cinnamic and benzoic acids that represent the building blocks for many pigments of higher fungi. Condensation of two arylpyruvic acid yields red to brown terphenylquinones and related orange to red grevillins. Diarylcyclopentenones, responsible for the colour changes in some bruised mushrooms, are formed by ring contractions of terphenylquinones while oxidative cleavage of the hydroxyquinone ring in terphenylquinones and rearrangement of thus formed intermediates results in a series of yellow and orange lactones known as pulvinic (pulvic) acids. Their decarboxylation yields the yellow pulvinones that can be oxidised and further transformed to a number of structurally related products. Reduction of cinnamic acids affords the corresponding alcohols that are the building blocks of benzotropolone pigments. Tyrosine, hydroxylated to 3,4-dihydroxyphenylalanine (DOPA), is the precursor of the red-violet betacyanins and the orange-yellow betaxanthins. Both amino acids and their transformation products can be converted via quinones into the heterogeneous dark pigments melanins by the enzymatic browning reactions (oxidations and polymerisations). Tryptophan is transformed to hydroxyanthranilic acids that become the precursor of phenoxazines and other nitrogen-containing pigments. Benzoquinones can be synthesised from very different starting substances and via different biochemical pathways, e.g. using benzoic acids produced in the shikimate pathway. Terpenoid quinones are formed by combination of the shikimate pathway with the mevalonate pathway. The polyketide pathway yields either aromatic ketides or fatty acids. For the aromatic ketides, the growing chain stabilises by cyclization reactions and partial reduction, whereas for fatty acids, the carbonyl groups of the chain are reduced before attachment of the next C_2 group. Products of this pathway include *tetra-*, *hepta-*, *octa-* and higher ketides and compounds of fatty acid origin. Fungi contain a range of pigments of octaketide origin (e.g. anthraquinones) that are based on the anthra-9,10-quinone skeleton with both rings substituted. In many cases, anthraquinones are found in fungi as the corresponding colourless reduced forms (anthranol, anthrone, anthrahydroquinone, and oxanthrone derivatives) that may occur in the form of various glycosides. Many natural anthraquinones are oligomers formed by coupling of two or more anthraquinone molecules. These oligomers further differ in the points through which monomers are attached and may have more than one polymorphic form (Velíšek *et al*. 2007, 2008; Velíšek & Cejpek 2008). Styrylpyrones are biosynthesised by a combined shikimate and polyketide pathway, which otherwise yields various terpenoids including carotenoids.

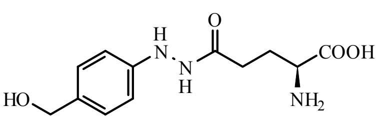
Various pigments and other fungi constituents show important biological activities (antioxidative, free radical scavenging, anticarcinogenic, immunomodulatory, antiviral, and antibacterial) that have generated intensive research interest (Steglich 1981; Calìa *et al*. 2003; Liu 2006; Medicinal Mushrooms 2008; Schüffler & Anke 2009).

The taxonomy of the kingdom Fungi (the subkingdom Dikarya) is in a state of constant flux; therefore, the most recent 2007 classification adopted by a coalition of mycologists was used (Thorna *et al*. 2007; MycoBank 2010). Out of seven phyla (divisions) proposed, the concern of this review only deals with the phylum Basidiomycota ("club fungi")[1] (subphylum Agaricomycotina, class Agaromycetes, subclass Agaromycetidae) that covers most of the so called "higher fungi" often referred to as "mushrooms"growing in Europe. The referred pigments, not reviewed up to now, are arranged according to the mushroom orders. Many other pigments were identified in fungi indigenous to Australasia.

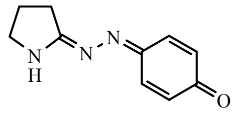
1 Agaricales

The genera *Agaricus* L., *Leucoagarius* Locq. ex Singer and *Macrolepiota* Singer of the Agaricaceae, including the common mushroom *A. bisporus* (J.E. Lange) Imbach (now cultivated in at least 70 countries around the world), contain the glutamic acid derived hydrazine agaritine (**1**) that may be enzymatically oxidised at the C-4 hydroxymethyl group to the corresponding formyl and carboxyl deriva-

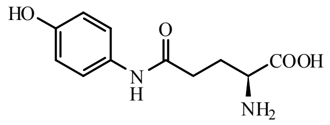
[1]The clade containing Ascomycota and Basidiomycota is classified as subkingdom Dikarya. The phylum Ascomycota ("sac fungi") covers some higher fungi (belonging to the subdivision Pezizomycotina, class Pezizomycetes, subclass Penzizomycodidae, order Pezizales), such as the true morel (*Morchella* Dill. ex Pers., Morchellaceae), the false morel (*Gyromitra* Fr., Discinaceae) and the truffle (*Tuber* P. Micheli ex F.H. Wigg., Tuberaceae). Their pigments have been studied only sporadically; the black pigments of the black truffle *T. melanosporum* are polymeric allomelanins of polyketide origin (De Angelis *et al*. 1996).



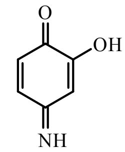
1. agaritine



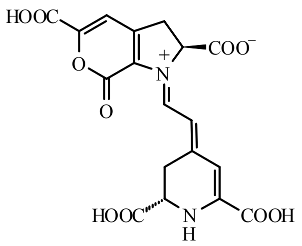
2. agaricone



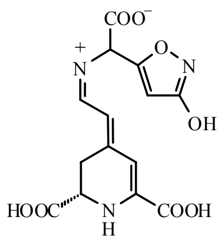
3. γ-glutamyl-4-hydroxybenzene



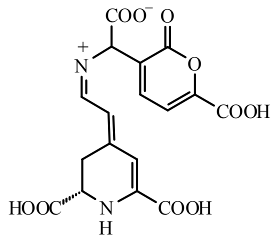
4. 2-hydroxy-4-imino-cyclohexa-2,5-dienone



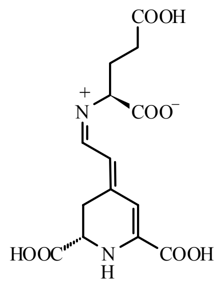
5. muscapurpurin



6. muskaaurin I



7. muskaaurin II

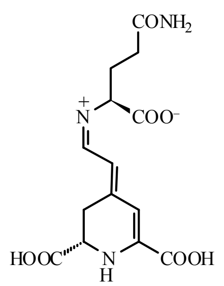


8. vulgaxanthin I

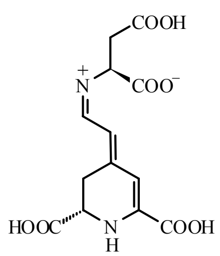
tives, which are hydrolysed to 4-(hydroxymethyl)-phenylhydrazine and 4-carboxymethylbenzoic acid, respectively. 4-(Hydroxymethyl)phenylhydrazine is oxidised to the corresponding diazonium cation. The metabolic fate of agaritine has been linked with the carcinogenity of the mushroom (Walton *et al.* 2001). The yellow pigment characteristic of the yellow-staining *A. xanthodermus* Genev. and of some other *Agaricus* species is caused by another azaquinone metabolite agaricone (**2**) that forms by oxidation of the corresponding leucophenol in the damaged tissue. The agaritine analogues derived from 4-aminophenol γ-glutamyl-4-hydroxybenzene (**3**) readily oxidise to the corresponding quinone *via* γ-glutamyl-3,4-dihydroxybenzene. This quinone decomposes to 2-hydroxy-4-iminocyclohexa-2,5-dienone (**4**), which imparts a pink-red colour to some agarics (e.g. to *A. bisporus*) (Hanson 2008a,b).

The striking orange-red pigments of the cap of fly agaric *Amanita muscaria* (L.) Hook. (*Amanita* Pers., Amanitaceae) are a mixture of the purple betacyanin muscapurpurin (**5**), orange betaxanthins muscaurins (muscaaurins) I–VII (**6** and **7**) and yellow muscaflavin (**12**). Muscaurin I (**6**) and muscaurin II (**7**) are derived from unusual nonprotein amino acids ibotenic acid and stizolobic acid, respectively, and are the major agaric pigments. Pigments named muscaurins III–VII are mixtures of pigments derived from common proteno-genous amino acids. Muscaurin III is a mixture of vulgaxanthin I (**8**), known as (*S*)-glutamine-betaxanthin, miraxanthin III (**9**), known as (*S*)-aspartic acid-betaxanthin, and a betaxanthin derived from 2-aminoadipic acid. Muscaurin IV is a mixture of vulgaxanthin I and miraxanthin III. Muscaurin V is a mixture of vulgaxanthin II (**10**), known as (*S*)-glutamic acid-betaxanthin, indicaxanthin (**11**), known as (*S*)-proline-betaxanthin, and betaxanthins derived from valine and leucine. Muscaurin VI is a mixture of vulgaxanthin II and indicaxanthin. Muscaurin VII is derived from histidine (Muso 1976; Li & Oberlies 2005).

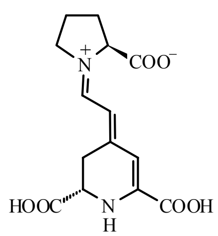
Fly agaric and mushrooms of the genus *Hygrocybe* (Fr.) P. Kumm. (Hygrophoraceae), e.g. *H. conica* (Schaeff.) P. Kumm., commonly known as the witch's hat, synthesise the yellow pigment muscaflavin (**12**),



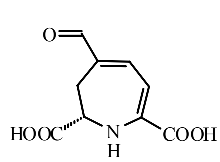
9. miraxanthin III



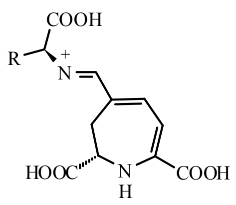
10. vulgaxanthin II



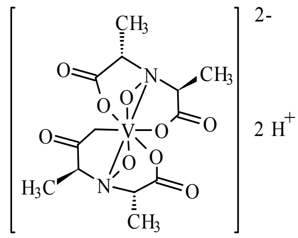
11. indicaxanthin



12. muscaflavin



13. hygroaurins (R = amino acid residue)



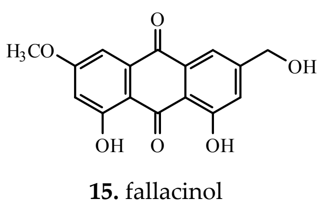
14. amavadin

derived from dihydroazepine, and store it in the cup skin. Analogously to betalamic acid involved in the formation of betalains, muscaflavin can spontaneously condense with amino acids, under the formation of aldimine bonds, yielding yellow hygroaurins (**13**) (Muso 1976; Li & Oberlies 2005).

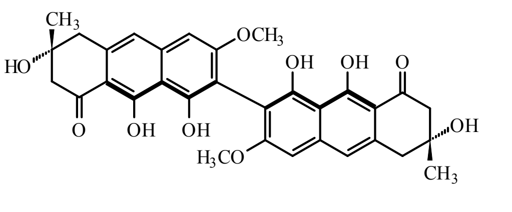
The unusually high concentration of vanadium in some *Amanita* species is ascribed to the formation of amavadin (**14**), a pale blue complex (1:2) of vanadium V^{4+} with (2*S*,2´*S*)-*N*-hydroxyimino-2,2'-dipropionic acid, isolated originally from *A. muscaria* (Bayer & Kneifel 1972).

The genus *Cortinarius* (Pers.) Gray (Cortinariaceae) represents the largest genus of agarics, containing about 1000 different species in Europe and found worldwide together with the closely related genera Dermocybe (Fr.) Wünsche (Cortinariaceae) and *Tricholoma* (Fr.) Staude (Tricholomataceae). A range of anthraquinones and biogenetically related metabolites has been found in these mushrooms principally due to the activity in the study of the Australian *Cortinarius/Dermocybe* species. The major dark orange pigment of the European toadstool *C. cinnabarinus* Fr. is fallacinol (6-*O*-methoxycitreorosein, **15**) (Gill & Steglich 1987; Gill 1994). Several species of the genera *Cortinarius*, *Dermocybe* and *Tricholoma*, such as *C. cinnamomeoluteus* P.D. Orton and *T. equestre* (L.) P. Kumm. (trivially known as Man on Horseback), produce a bright yellow dimeric anthraquinone flavomannin-6,6'-di-*O*-methyl ether (**16**). This pigment is biosynthesised by 7,7'-coupling of the corresponding green dihydroanthracenone (3*R*)-torosachrysone (**17**). In its homochiral form it also occurs in the European *C. citrinus* J.E. Lange ex P.D. Orton and *C. croceus* (Schaeff.) Gray, while in Australian fungi it forms as a mixture of (3*R*,3*R*',*M*)- (**16**) and (3*R*,3*R*',*P*)-atropoisomers. The green (3*R*)-atrochrysone (**17**) occurs in *C. atrovirens* Kalchbr. and *C. odoratus* (M.M.Moser) M.M.Moser, (3*S*)-torosachrysone-8-*O*-methyl ether in *C. fulmineus* (Fr.) Fr., *C. citrinus* J.E. Lange ex P.D. Orton, *C. splendens* R. Henry, *T. equestre* (L.) P. Kumm. and the Sulphur Knight *T. sulphureum* (Bull.) P. Kumm. (Gill & Steglich 1987; Gill 1994). A number of anthraquinone pigments formally derived from torosachrysone and atrochrysone by coupling (dimeric, trimeric and tetrameric octaketides) have been described, mostly in Australian fungi belonging to the genera *Cortinarius*, *Dermocybe* and, to a lesser extent, *Tricholoma* (Gill & Morgan 2001).

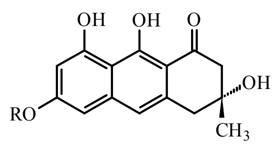
The European members of the genus *Cortinarius* characteristically contain the xanthone dermoxanthone (**18**) and its methyl ester that were found in the stem of the Surprise Webcap *C. semisanguineus* (Fr.) Gill. These xanthones are responsible for the bright yellow fluorescence under UV light (Gill 1999). The fruiting bodies of several *Cortinarius* species, such as the Violet Webcap *C. violaceus* (L.) Gray, have a strikingly deep violet colour of the fruiting bodies, which is ascribes to the unique β-DOPA-Fe^{3+} complex $[Fe^{3+}L_2(H_2O_2)]^-$ or $[Fe^{3+}L_4(H_2O_2)]^{2-}$, where L is the (3*R*)-β-DOPA anion ligand (**19**). These mushrooms concentrate iron by as much as 100-fold over other Basidiomycota (Von Nussbaum *et al*. 1998). Unusually high concentrations of iron were also found in the Velvet Bolete, *Suillus variegatus* (Sw.) Kuntze (Boletales) (Drbal *et al*. 1975; Kalač *et al*. 1989).



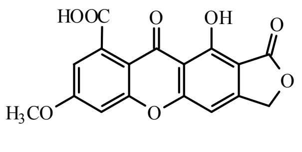
15. fallacinol



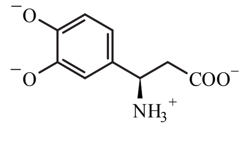
16. (3*R*,3*R*',*M*)-flavomannin-6,6'-di-*O*-methyl ether



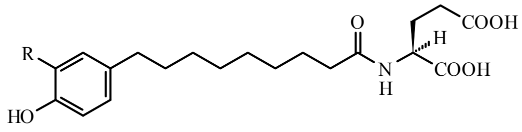
17. (3*R*)-atrochrysone, R = H
(3*R*)-torosachrysone, R = CH_3



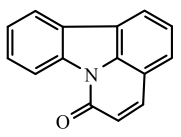
18. dermoxanthone



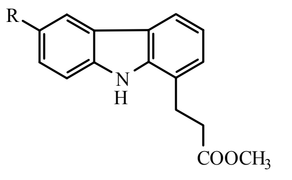
19. β-DOPA anion



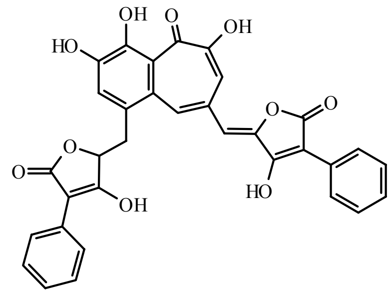
20. scaurin A, R = H
scaurin B, R = OH



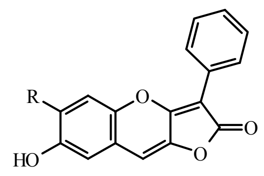
21. canthin-6-one



22. infractin A, R = H
infractin B, R = OH



23. aurantricholone



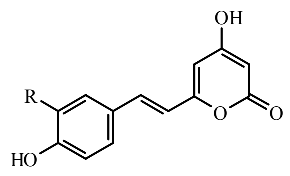
24. aurantricholide A, R = OH
aurantricholide B, R = H

Scaurins (**20**) are the polyene pigments with bound glutamic acid that were isolated from the fruiting bodies of *C. scaurus* (Fr.) Fr. (Gill 1998, 2003). Alkaloids containing the canthin-6-one skeleton are produced by some other *C.* species. The parent compound canthin-6-one (**21**) occurs in the bitter-tasting *C. infractus* (Pers.) Fr. together with the β-carboline derivatives infractin A and B (**22**) (Gill 1996).

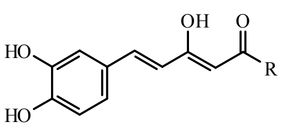
The benzotropolone derivative aurantricholone (**23**), isolated from the bright orange-red caps of *Tricholoma aurantium* (Schaeff.) Ricken, is closely related to the naphthalenoid pulvinic acid badione A occurring in the Boletales mushrooms (see Chapter 2). It occurs naturally as a metal chelate; the predominant counter ion is calcium (Klostermeyer *et al*. 2000). Minor pigments are the yellow aurantricholides A and B (**24**).

The yellow-brown styrylpyrone pigments bisnoryangonin and hispidin (**25**) are widespread among fungi of the Strophariaceae family, genera *Gymnopilus* P. Karst., *Hypholoma* (Fr.) P. Kumm. and *Pholiota* (Fr.) P. Kumm., where they have a considerable taxonomic significance (Gill 1994). Hispidin is biosynthesised by two different mechanisms using the activated 4-hydroxy-6-methylpyrone (a condensation product of three activated acetates) and the activated 3,4-dihydroxybenzoic acid or from phenylalanine *via* a cinnamyl derivative that is combined with either acetate or malonate through the polyketide pathway. The related open chain β-keto ester (**26**, R = $COOCH_3$) was isolated some years ago as the Brick Cap *H. sublateritium* (Schaeff.) Quél. pigment. The yellow pigment hispolon is the hydrolytic and decarboxylation product of the open chain β-keto ester (**26**) (Gill 1994). It also occurs in mushrooms of the Hymenochaetaceae family, e.g. in several *Inonotus* P. Karst., *Onnia* P. Karsten and *Phellinus* Quél. species. (Lee & Yun 2006)

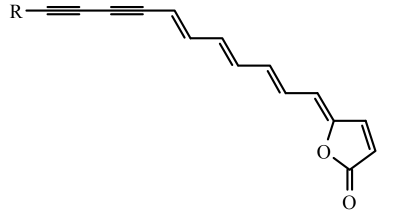
Orange-yellow polyenes of fatty acid origin, dihydroxerulin, xerulin and xerulinic acid (**27**), are the pigments of *Oudemansiella melanotricha* (Dörfelt) M.M. Moser (*Oudemansiella* Speg.,



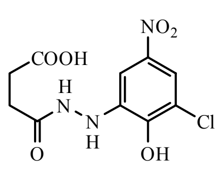
25. bisnoryangonin, R = H
hispidin, R = OH



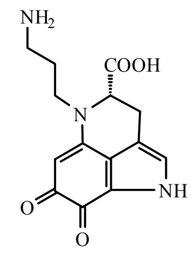
26. hispolon, R = CH_3



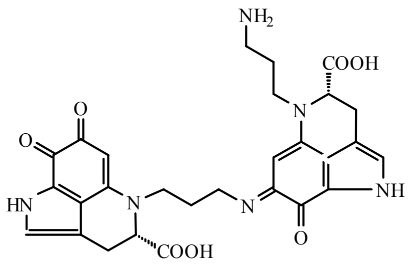
27. dihydroxerulin, R = CH_2-CH_2-CH_3
xerulin, R = CH=CH-CH_3
xerulinic acid, R = CH=CH- COOH



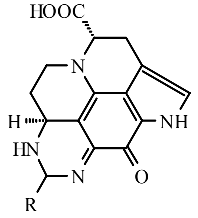
28. stephanosporin



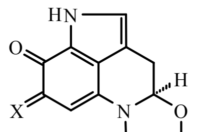
29. mycearubin A



30. mycearubin B



31. sanguinone A, R = H
sanguinone B, R = CH_3



32. haematopodin, X = O
haematopodin B, X = NH

Physalacriaceae) that act as inhibitors of cholesterol biosynthesis (Kuhnt *et al.* 1990).

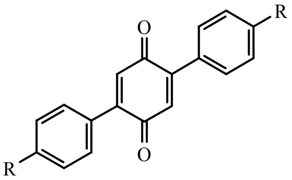
The carrot truffle, *Stephanospora caroticolor* (Berk.) Pat. (*Stephanospora* Pat., Stephanosporaceae), contains in its subterranean tuber-like fruiting bodies the pigment stephanosporin (**28**). This unusual hydrazine derivative is biosynthesised using 2-chloro-4-nitrophenol as the building block. Both compounds occur naturally as their potassium salts and are responsible for the bright orange colour of the mushroom (Lang *et al.* 2001).

The pyrroloquinone alkaloids isolated from *Mycena* (Pers.) Roussel (Mycenaceae) species include the red pigments mycearubin A (**29**), mycearubin B (**30**) and related compounds from the fruiting bodies of *M. rosea* (Schumach.) Gramberg (Peters & Spiteller 2007a) and the Bleeding Fairy Helmet *M. haematopus* (Pers.) P. Kumm. The blue sanguinones A and B (**31**) were isolated from *M. sanguinolenta* (Alb. & Schwein.) P. Kumm. (Peters & Spiteller 2007b) and red haematopodins from the fragile reddish-brown stems of *M. haematopus* (Hopmann & Steglich 2006; Peters *et al.* 2008). These alkaloids are exemplified by the minor pigment haematopodin (**32**), a breakdown product of the labile red haematopodin B (**32**), which is the main pigment of the mushroom decomposing under the influence of air and light (Hopmann & Steglich 2006).

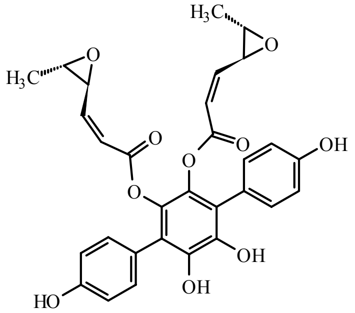
2 Boletales

Mushrooms of the order Boletales are characterised by a diversity of colours mainly derived from terphenylquinones and pulvinic acids. Terphenylquinones, exemplified by polyporic acid (**33**) and atromentin (**33**), are mainly produced by wood-rotting higher fungi of the order Polyporales growing on various deciduous trees but in other higher fungi, such as in the Boletales fungi, they only appear sporadically. However, atromentin is their key intermediate for many conversions leading to more highly hydroxylated terphenylquinones, hydroxypulvinic acids, cyclopentenones and related compounds. In the intact fruit bodies, atromentin occurs in the form of its colourless precursors leucomentins.

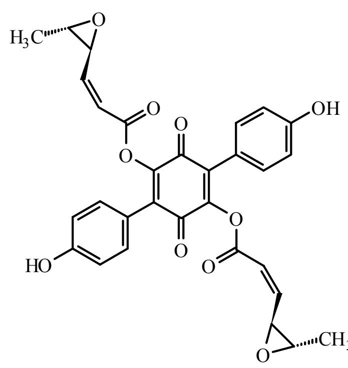
Leucoderivative of atromentin esterified with (2*Z*,4*S*,5*S*)-4,5-epoxyhex-2-enoic acid from the lignicolous fungi *Tapinella atrotomentosa* (Batsch) Šutara (*Tapinella* E.-J. Gilbert, Tapinellaceae) sporophore is leucomentin-2 (**34**) (Gill & Steglich 1987; Gill 1994; Liu 2006; Hanson 2008b). This



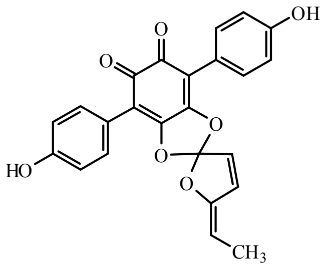
33. polyporic acid, R = H
atromentin, R = OH



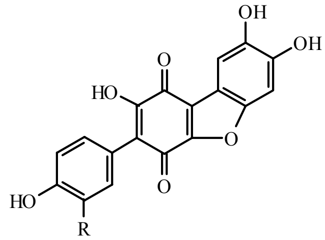
34. leucomentin-2



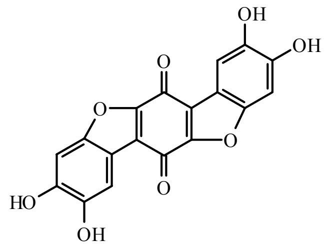
35. flavomentin A



36. spiromentin A



37. cycloleucomelone, R = H
cyclovariegatin, R = OH



38. thelephoric acid

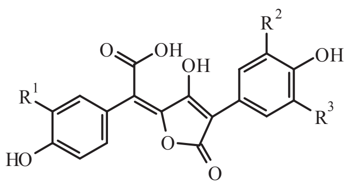
compound and leucomentin-3, -4, -5 and -6 were found in a number of other fungi. Mushrooms of the genus *Tapinella* also produce small amounts of orange-yellow flavomentins A-D and violet spiromentins A-D (spiromentins E-J, derivatives of benzene-1,2,4,5-tetraol, are colourless) derived from atromentin. The flavomentins constitute diesters and monoesters of atromentin with (2*Z*,4*S*,5*S*)-4,5-epoxyhex-2-enoic and (2*Z*,4*E*)-hexa-2,4-dienoic acids. The spiromentins possess a unique spiro structure in which a 4,5-dihydroxybenzo-1,2-quinone is linked to a lactone acetal unit (Besl *et al.* 1989). Flavomentin A (**35**) and spiromentin A (**36**) exemplify these metabolites.

Simple oxidation products of terphenylquinones under the preservation of the central quinone ring include cycloleucomelone (**37**) and cyclovariegatin (**37**), which is the precursor of the violet thelephoric acid (**38**). Cycloleucomelone occurs in the fruiting bodies of *Boletopsis leucomelaena* (Pers.) Fayod (*Boletopsis* Henn., Suillaceae) (Jägers *et al.* 1987) and is accompanied by a series of colourless analogues containing five, four and three acetyl residues. Cyclovariegatin occurs in this mushroom as the colourless peracetate of the leucoform (Edwards & Gill 1973).

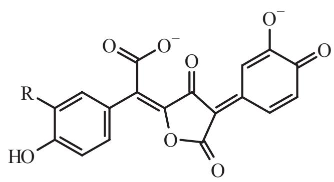
The major pigments of the order Boletales are the yellow pulvinic acids (**39**) that are formed through lactone formation, after the terphenylquinone ring has been oxidized and opened. The unsubstituted parent compound, pulvinic acid, only occurs in the form of its methyl ester named vulpinic acid. Xerocomic and variegatic acids play the most important role being responsible for the blue colours acquired in many boletes after their fruiting bodies are injured, which results in the oxidation of these acids to the corresponding blue chinonmethid anions (**40**). Pulvinic acids are especially widespread in mushrooms belonging to the Gomphidiaceae and Suillaceae families, to the genera *Gomphidius* Fr. and *Suillus* Gary. The yellow pigment gomphidic acid (**39**) was found for the first time in the Slimy Spike-cap *G. glutinosus* (Schaeff. ex Fr.) Fr. (Knight & Pattenden 1976).

The yellow-brown cap and stem of the Larch Bolete *Suillus grevillei* (Klotzsch) Sing. contain at least 11 yellow, orange and red pigments derived from decarboxylated pulvinic acids, of which 3',4',4-trihydroxypulvinone (**41**) is the major pigment (Besl & Bresinsky 1997). Cyclovariegatin (**37**) is also partly responsible for its colour (Edwards & Gill 1973).

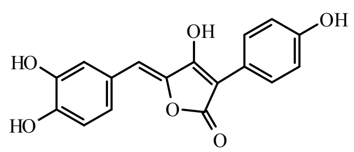
In the pathway leading to atromentin, instead of two C-C bonds only one C-C bond may be formed. The resulting lactonisation then yields grevillins (**42**). Grevillins A, B, C and D are a group of characteristic orange to red 2*H*-pyran-2,5(6*H*)dione pigments that occur only in the fruiting body of



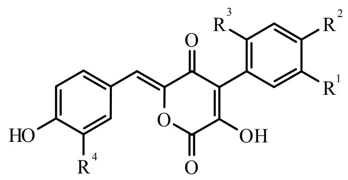
39. atromentic acid, $R^1 = R^2 = R^3 = H$
xerocomic acid, $R^1 = H$, $R^2 = OH$, $R^3 = H$
gomphidic acid, $R^1 = H$, $R^2 = R^3 = OH$
isoxerocomic acid, $R^1 = OH$, $R^2 = R^3 = H$
variegatic acid, $R^1 = OH$, $R^2 = OH$, $R^3 = H$



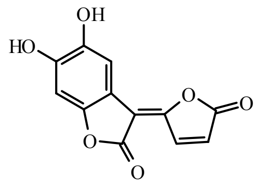
40. chinonmethid anion of xerocomic acid, R = H
chinonmethid anion of variegatic acid, R = OH



41. 3',4',4-trihydroxypulvinone



42. grevillin A, $R^1 = R^3 = R^4 = H$, $R^2 = OH$
grevillin B, $R^1 = R^3 = H$, $R^2 = R^4 = OH$
grevillin C, $R^1 = R^2 = R^4 = OH$, $R^3 = H$
grevillin D, $R^1 = R^3 = R^4 = OH$, $R^2 = H$



43. gomphilactone

mushrooms belonging to the genus *Suillus* Gray. *S. grevillei* (Klotzsch) Sing. and *S. luteus* (L. ex Fr.) S. F. (Slippery Jack) contain grevillins A, B and C, *S. granulatus* (L. ex Fr.) O. Kuntze (Weeping Bolete) contains grevillins B, C and D, of which the major pigment is grevillin D (Besl *et al.* 1974).

The colourless, but easily oxidisable 1,2,4-trihydroxybenzene and its derivatives commonly occur in mushrooms belonging to the Gomphidiaceae family and to the genus *Suillus* Gray. The oxidation products of 1,2,4-trihydroxybenzene include the red gomphilactone (**43**) and the corresponding biphenyls. Variegatorubin (**44**) and xerocomorubin (**44**) exemplify the red pigments formed from pulvinic acids by the second lactone ring production (Besl & Bresinsky 1997).

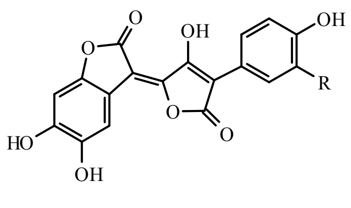
High concentrations of radionuclides occurring in the fruiting bodies of the Bay Bolete *Boletus badius* (Fr.) Fr. (*Boletus* Fr., Boletaceae) after the nuclear reactor accident at Chernobyl have been ascribed to the complexation of ^{137}Cs by the so called naphthalenoid pulvinic acids that occur as their potassium salts in the cap skin of this toadstool. The main compounds are badione A (**45**) and norbadione A (**46**) that are responsible for the chocolate brown and golden yellow colours of cap skin of this bolete and related bolete species (Aumann *et al.* 1989).

Norbadione A (**46**) is the dominating compound in the dying mushroom *Pisolithus arrhizus* (Scop.) Rauschert (*Pisolithus* Alb. & Schwein, Sclerodermataceae) where it occurs in amount of over 25% of the dry weight of the fungus. Badione A (**45**) and several similar compounds are minor components (Winner *et al.* 2004).

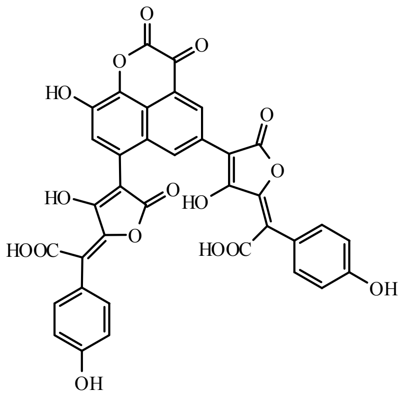
Oxidative coupling of two molecules of xerocomic acid (**39**) yields bright yellow sclerocitrin (**47**) occurring in the fruiting bodies of the common Earth Ball *Scleroderma citrinum* Pers. (*Scleroderma* Pers., Sclerodermataceae) together with norbadione A (**46**) as the main pigments, which are accompanied by xerocomic acid (**39**) and badione A (**45**) (Winner *et al.* 2004).

Sclerocitrin is the main pigment of the lemon-yellow coloured stalk base of the Peppery Bolete *Chalciporus piperatus* (Bull.) Bataille (*Chalciporus* Bataille, Boletaceae). It is accompanied by the second yellow pigment chalcitrin (**48**), norbadione A (**46**), variegatic acid (**39**) and variegatorubin (**44**) (Winner *et al.* 2004).

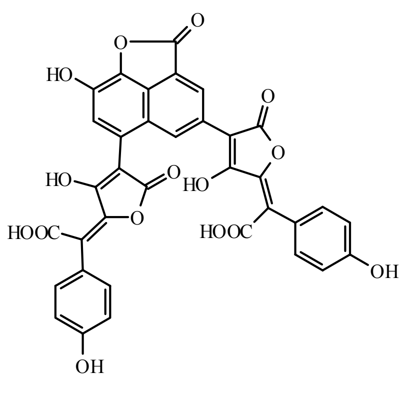
The decarboxylation products of pulvinic acids, 2,5-diarylcyclopentenones, appear in fungi almost as frequently as terphenylquinones. Typical examples are chamonixin (**49**), involutin (**49**) and the more highly oxidised gyrocyanin (**50**) and gyroporin (**50**).



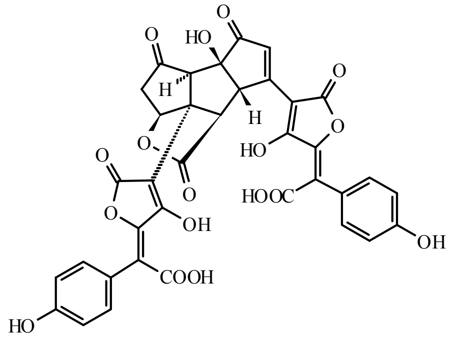
44. xerocomorubin, R = H
variegatorubin, R = OH



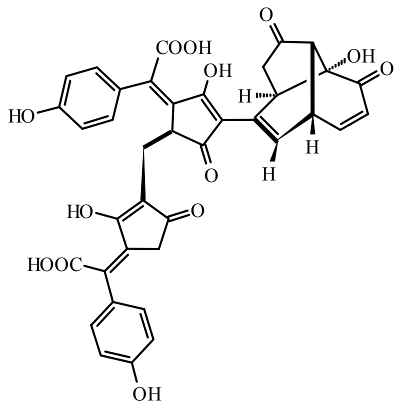
45. badione A



46. norbadione A



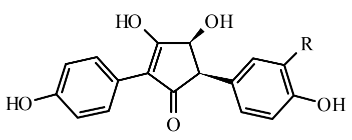
47. sclerocitrin



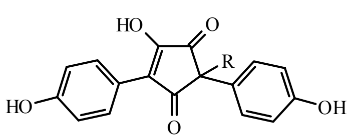
48. chalcitrin

They occur e.g. in several families of Boletales, in the genera *Chamonixia* Rolland (Boletaceae), *Gyrodon* Opat. (Paxillaceae), *Gyroporus* Quél. (Gyroporaceae), *Leccinum* Gray (Boletaceae), *Melanogaster* Corda (Melanogasteraceae), *Paxillus* Fr. (Paxillaceae) and several other families and genera. The pigments are responsible for the conspicuous deep brown and bright blue colour reactions observed when the fruiting bodies of mushrooms are bruised. Involutin occurs in *P. involutus* (Batsch ex Fr.) Fr. (chamonixin is a minor compound); chamonixin is a constituent in *C. caespitosa* Rolland and gyrocyanin in *G. cyanescens* (Bull. ex Fr.) Quél. The colour changes of the latter mushroom are associated with the related metabolite of gyrocyanin, which is oxidised to the blue anion (**51**) (Feling *et al.* 2001; Hanson 2008b).

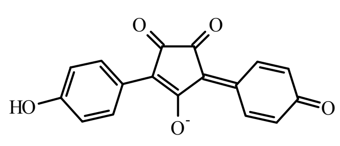
The prenylated compounds occur only rarely in Boletales being biosynthesised from 3,4-dihydroxybenzoic acid (Besl & Bresinsky 1997). The aromatic ring often bears an additional farnesyl or geranylgeranyl side-chain derived from the terpenoid pathway. Suillin (**52**) is an example of acetylated and prenylated 1,2,4-trihydroxybenzene that occurs in *S. granulatus* (L. ex Fr.) O. Kuntze. Its oxidation products are responsible for the caps' brown colour. Prenylated benzoquinones, corresponding to 1,2,4-trihydroxybenzene (mentioned above), mostly appear as meroterpenoids named boviquinones. Boviquinone-3 (2,5-dihydroxy-3-farnesyl-1,4-benzoquinone) is biosynthesised by *Chroogogompus rutilus* (Schaeff.) O.K. Mill., *Chroogomphus* (Singer) O.K. Mill. (Gomphidiaceae), bovinoquinone-4 (2,5-dihydroxy-3-geranylgeranyl-1,4-benzoquinone, **53**) is an example of prenylated benzoquinones found in *Suillus bovinus* (L.) Roussel. (Mühlbauer *et al.* 1998). The red pigment tridentoquinone (**54**) is the main pigment of *S. tridenticus (Bres.) Singer*, which is related to the linear boviquinone-4 (**53**) from *S. bovinus* (L.) Roussel. In the mushroom, tridentoquinone is accompanied by several compounds of similar structure (Lang *et al.* 2008). Mushrooms of the genus *Rhizopogon* Fr. (i.e. *Rhizopogon pumilionum* (Ade) Bataille), closely related to the genus *Suillus* Gray, contain rhizopogone (**55**) as the main pigment (Lang *et al.* 2009).



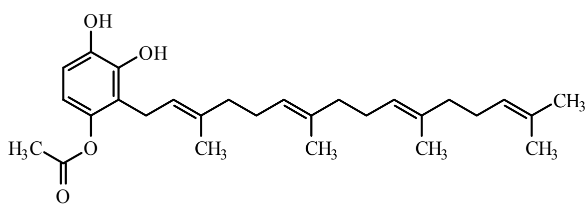
49. chamonixin, R = H
involutin, R = OH



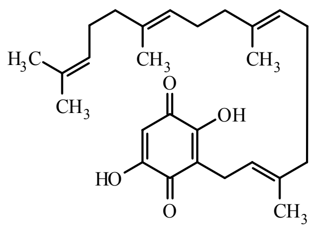
50. gyrocyanin, R = H
gyroporin, R = OH



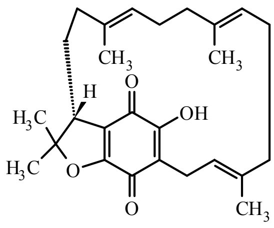
51. blue anion of gyrocyanin



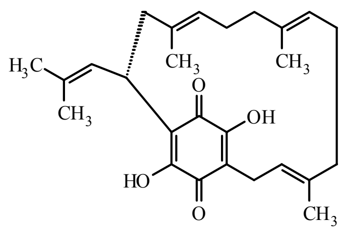
52. suillin



53. boviquinone-4



54. tridentoquinone



55. rhizopogone

Melanocrocin (**56**) is a unique brilliant yellow polyene pigment, with bound phenylalanine, isolated from the subterranean fungus *Melanogaster broomeianus* that resemble truffles (Aulinger *et al.* 2001).

3 Cantharellales

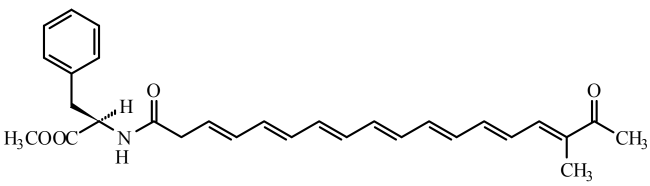
Carotenoids are not widespread in higher fungi as they are in plants; nevertheless, they were isolated from several yellow pigmented *Cantharellus* Juss. (Cantharellaceae) species. The Golden Chanterelle *C. cibarius* Fr. pigment mixture was found to consist mainly of β-carotene and also present were lycopene, α-carotene and two other carotenes, probably the γ- and δ-isomers or the xanthophyl canthaxanthin (**57**) that was found in the pink to red-orange Cinnabar Chanterelle *C. cinnabarinus* (Schwein.) Schwein. as the main pigment (Haxo 1950; Hanson 2008b).

4 Hymenochaetales

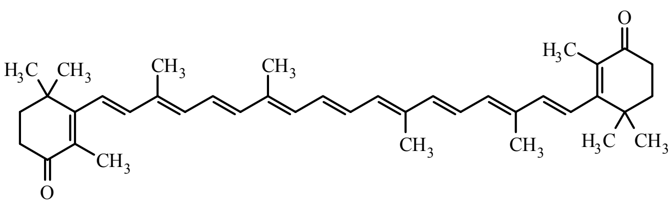
Styrylpyrone hispidin (**25**) was originally isolated as the main constituent of the plant pathogen the Chaga Fungus *Inonotus hispidus* (Bull.) P. Karst., the polypore with a red-brown fruiting body (Bu'Lock *et al.* 1962), where it is accompanied by bisnoryangonin (**25**), hypholomin B (**58**) and the yellow pigment hispolon (**26**, R = CH_3) (Ali *et al.* 1996). These pigments also occur in several mushrooms of the Hymenochaetaceae family, e.g. in *Inonotus* P. Karst., *Onnia* P. Karsten and *Phellinus* Quél. species and in the genus Hypholoma (Fr.) P. Kumm. of the Strophariaceae family (Agaricales). Inoscavin A, reported to be a free radical scavenger, isolated from the fruiting bodies of the mushroom *P. xeranticus* (Berk.) Pegler (*Phellinus*, Hymenochaetaceae) has been assigned the fused styrylpyrone structure (**59**), which relates inoscavin A closely to hispidin (**25**) and thence to hypholomin B (**58**).

5 Polyporales

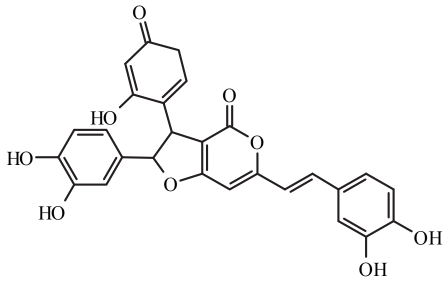
Species within the order Polyporales are saprotrophic and most of them wood-rotters. The Polyporaceae are a family of such wood-decay fungi that contain pigments mostly derived from polyporic acids and terphenylquinones. The dark red polyporic acid (**33**), the parent compound of numerous terphenylquinones and related compounds, is the major component of *Hapalopilus nidulans* (Fr.)



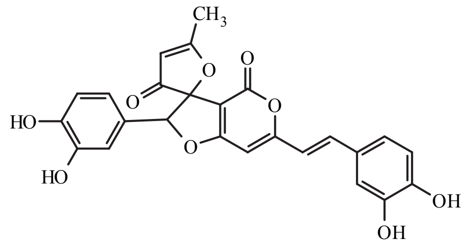
56. melanocrocin



57. canthaxanthin



58. hypholomin B



59. inoscavin A

P. Karst. (*Hapalopilus* P. Karst.) amounting up to 43% of its dry weight. Betulinans A (**60**) and B (**61**) are two simple terphenylquinones recently found in the plant pathogen *Lenzites betulina* (L.) Fr. (*Lenzites* Fr.) (Lee *et al.* 1996; Gill 1999). The labile 2,3,4-trihydroxycinnamyl alcohol is the building block of the purpurogallin (benzotropolone) derivative fomentariol (**62**) produced by the plant pathogen, the Tinder Fungus, *Fomes fomentarius* (L.) Fr. of the genus *Fomes* (Fr.) Fr. (Polyporaceae) (Steglich & Zechlin 1978).

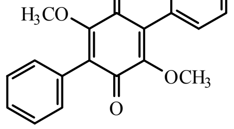
Pigments with a phenoxazine chromophore widely occur in lichens and to a smaller extent in higher fungi of the Polyporaceae family. The cinnabar red pigment of the wood-rotting fungus *Pycnoporus cinnabarinus* (Jacq.) P. Karst. (*Pycnoporus* P. Karst.) is 2-amino-3*H*-phenoxazin-3-one-1,9-dicarboxylic acid named cinnabaric acid (**63**). It is biosynthesized from 3-hydroxyanthranilic acid units formed as the tryptophan transformation products (Gripenberg 1958a).

The cobalt Crust Fungus *Terana caerulea* (Lam.) Kuntze (*Terana* Adans.) of the Phanerochaetaceae family contains corticins A (**64**), B and C as the colourless quinhydrones that are oxidized to the indigo-blue pigment in hymenal surface (Briggs *et al.* 1976). The saprophytic fungus *Phanerochaete sanguine* (Fr.) Pouzar (*Phanerochaete* P. Karst.) contains xylerythrin-type pigments (**65**). Their structures suggest a biosynthesis from three molecules of arylpyruvic acids. The wood infected by this fungus is then coloured dark red by its mycelium (Gripenberg 1965; Gripenberg & Martikkala 1970).

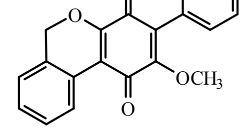
The striking yellowish or orange-coloured fruiting bodies of the wood-rotting edible mushroom *Laetiporus sulphurous* (Bull.) Murrill (*Laetiporus* Murrill), belonging to the Fomitopsidaceae family, contains non-isoprenoid polyene known as laetiporic acid A (predominantly occurring as the 7-*cis*-isomer, **66**) and 2-dehydro-3-deoxylaetiporic acid A (**67**) as the main pigments (Davoli *et al.* 2005).

6 Russulales

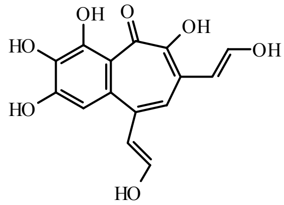
Apart from carotenoids, only a few lower terpenoids are coloured compounds. The colour of the injured flesh as well as of the latex of several *Lactarius Pers.* (Russulaceae) species own to their colour changes to sesquiterpenoids. The young fruiting body of *L. deliciosus* (L. ex Fr.) S. F. Gray is first carrot-coloured, but slowly turns green on aging. The young *L. deterrimus* Gröger fruiting body is pale peach coloured and becomes apricot coloured with a greyish green shades on aging. On cutting, *L. deterrimus* yields saffron or orange coloured latex. These colour changes are due to sesquiterpenoids derived from azulene. The compounds responsible for these colour changes in *L. deliciosus* are the blue lactarazulene, i.e. 1,4-dimethyl-7-(1-methylethenyl)azulene (**68**), and lipophilic red-violet lactaroviolin, i.e. 4-methyl-7-(1-methylethenyl)azulene-1-carbaldehyde (**68**). However, neither lactarazulene nor lactaroviolin occurs as such. The orange colour of the fungus is due to the labile and easily oxidizable dihy-



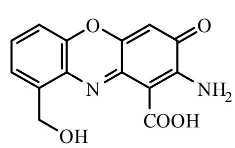
60. betulinan A



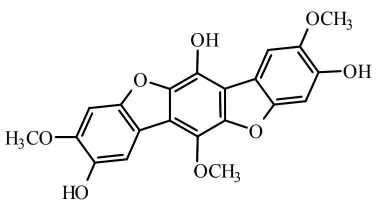
61. betulinan B



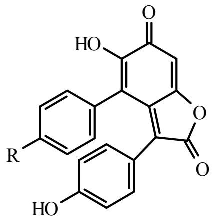
62. fomentariol



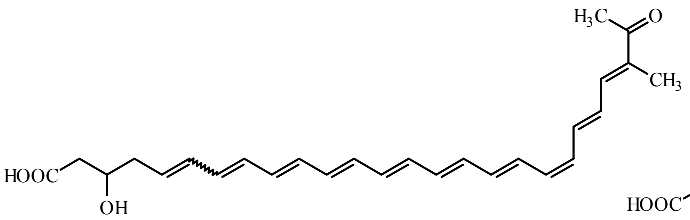
63. cinnabarinic acid



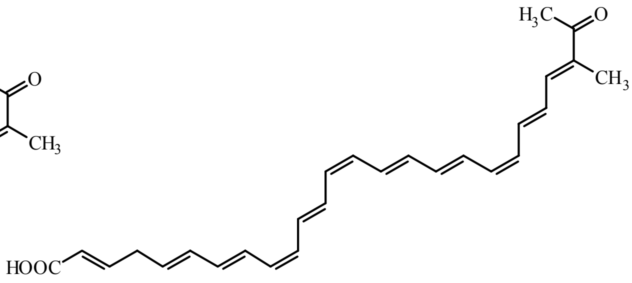
64. corticin A



65. xylerythrin, R = H
peniophorin, R = OH



66. laetiporic acid A



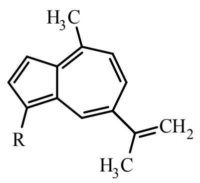
67. 2-dehydro-3-deoxylaetiporic acid A

droazulen-1-ol (**69**, R=H) or to their stearates, **69**, R = $CO[CH_2]_{16}CH_3$. Recently, three other red azulene pigments have been isolated from the fruiting bodies of *L. deliciosus* being 7-acetyl-4-methylazulene-1-carbaldehyde, 7-(1,2-dihydroxy-1-methylethyl)-4-methylazulene-1-carbaldehyde and 7-acetyl-4-methylazulene-1-carboxylic acid (Xang *et al.* 2006; Zhou & Liu 2010). The red pigment 1,3,5,7(11),9-pentaenyl-14-guaianal (**70**) was found in *L. sanguifluus* (Paulet) Fr., the lipophilic pigment 1-hydroxymethyl-4-methyl-7-(1-methylethenyl)azulene stearate; **68**, R = $CH_2OCO[CH_2]_{16}CH_3$, is responsible for the brilliant blue colour of the Indigo Milk Cap *L. indigo* (Schwein.) Fr. (native to America and Asia and also reported from southern France) (Harmon *et al.* 1980; Ayer & Browne 1981; Koul *et al.* 1985; De Rosa & De Stefano 1987).

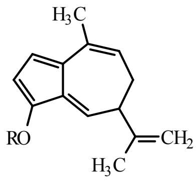
The milky juice of *L. scrobiculatus* (Scop.) Fr. turns rapidly from white to yellow. A range of lactarane and secolactarane sesquiterpenoids, analogues of the above azulenes, have been isolated (Bosetti *et al.* 1989). The structures of uvidin A and B (**71**) illustrate the broad variety of compounds found in *L. uvidus* (Fr.) Fr. Drimane sesquiterpenoids like drimenol (**72**) and uvidins have so far been found only in *L. uvidus*, which has a white latex rapidly turning violet on exposure to the air.

Intact fruiting bodies of *Lactarius fuliginosus* (Krapf) Fr. and *L. picinus* Fr. contain the isoprenoid quinol stearate of 4-methoxy-2-(3-methylbut-2-enyl)phenol (**73**). The pink-red stain and acrid taste that develops when the toadstool is bruised are due to its hydrolysis followed by oxidation to a variety of red benzofurans and chromenes (De Bernardi *et al.* 1992).

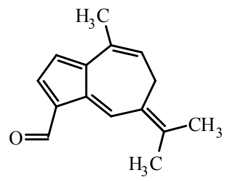
The pale green aminobenzoquinone blennione (**74**) occurs in the fruit bodies of the common toadstool, the Slimy Milkcap *Lactarius blennius* (Fr.) Fr. It is probably biosynthesized using 3,6-dihydroxyanthranilic acid units (Spiteller & Steglich 2002). Biosynthetically closely related to bennione is the red pigment lilacinone (**75**), which is responsible for the violet colour of *Lactarius lilacinus* (Lasch) Fr. (Spiteller *et al.* 2003).



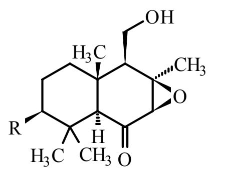
68. lactarazulene, R = CH_3
lactaroviolin, R = CH=O



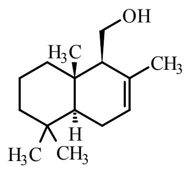
69. dihydroazulen-1-ol (R = H)



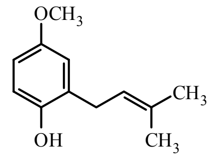
70. 1,3,5,7(11),9-pentaenyl-14-guaianal



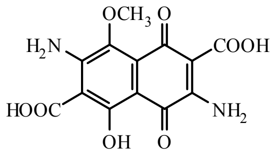
71. uvidin A, R = H
uvidin B, R = OH



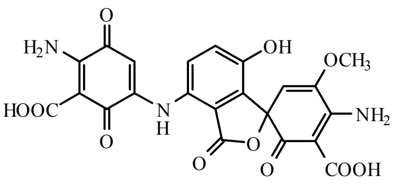
72. drimenol



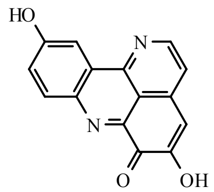
73. 4-methoxy-2-(3-methylbut-2-enyl)phenol



74. blennione



75. lilacinone



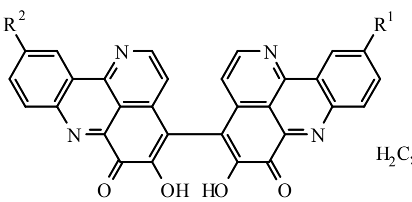
76. necatarone

An alkaloidal pigment necatarone (**76**), its dehydrodimer (**77**, $R^1 = R^2 = OH$) prevailing in aged fruiting bodies and the 10-deoxydehydrodimer (**77**, $R^1 = H$, $R^2 = OH$) are the principal pigments of the green-brown flesh and cap skin of *Lactarius turpis* (Weinm.) Fr. (Fugmann *et al.* 1984, Klamann *et al.* 1989).

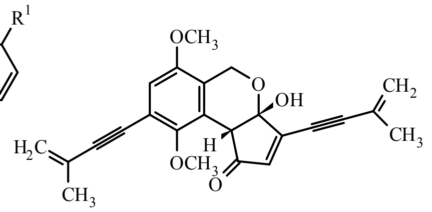
Ochroleucins are the main pigments of the fruiting bodies of the Common Yellow Russula, *Russula ochroleuca* Pers. and *R. viscida* Kudrna (*Russula* Pers., Russulaceae). The labile yellow ochroleucin A (**78**) is rapidly transformed to the stable red ochroleucin B (**79**) (Sontag *et al.* 2006).

Dimeric meroterpenoid pigments have been reported from the *Albatrellus* Gray species (Albatrellaceae), which included e.g. the purple pigment grifolinone B (**80**), the red ketone albatrellin (**81**) and a variety of related compounds of the mushroom *A. confluens* (Alb. & Schwein.) Kotl. & Pouzar (Yang *et al.* 2008).

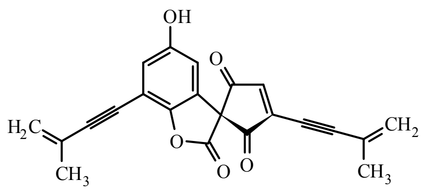
The Orange Tooth *Hydnellum aurantiacum* (Batsch) P. Karst. (*Hydnellum* P. Karst., Peniophoraceae) colour is derived from the terphenylquinone atromentin. The 3,6-dibenzoylatromentin, named aurantiacin, was first isolated as a dark red pigment from this mushroom and subsequently from various *Hydnellum* species (Gripenberg 1956; Gripenberg 1958b). Aurantiacin is accompanied with the corresponding leucoform dihydroaurantiacin and thelephoric acid.



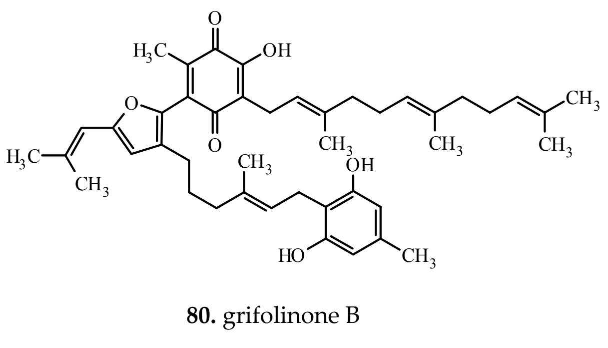
77. necatarone dehydrodimer



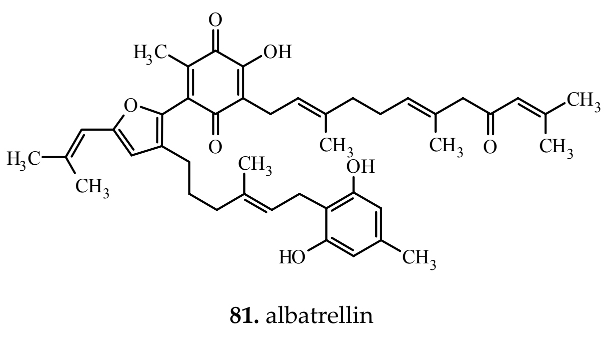
78. ochroleucin A



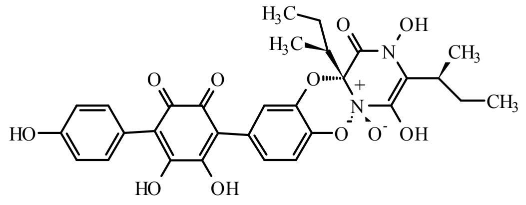
79. ochroleucin B



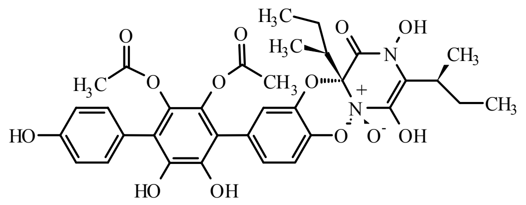
80. grifolinone B



81. albatrellin



82. sarcoviolin α



83. sarcodonin α

7 Thelephorales

The fruiting bodies of *Sarcodon leucopus* (Pers.) Maas Geest. & Nannf. (*Sarcodon* Quél. ex P. Karst., Bankeraceae) contain a range of compounds related to terphenylquinones. The main pigments are the unusual nitrogenous violet terphenylquinols sarcoviolins, exemplified by sarcoviolon α (**82**), which are accompanied by their colourless precursors sarcodonins (**83**) and structurally related compounds (Geraci *et al.* 2000; Cali *et al.* 2004).

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