CH–), 4·50 (1H, doublet, J 2·5 Hz, –CO.CHOH.CHOH–, 5·08 (1H, doublet, J 2·5 Hz, –CO.CHOH.CHOH–), 6·38 (1H, singlet, –C=CH–), 6·71 (1H, doublet, J 17 Hz, trans CH=CH–), 7·09 (1H, octet, J 17 and 6 Hz, Me CH=CH–), in the presence of Na_2CO_3, the peak at δ 5·08 disappeared (keto-enolic H). CMR (D_2O); the peak patterns after removal of the off-resonance proton decoupler are shown in parenthesis: δ 19·7 (C-8; quartet), 77·0 (C-3; doublet), 81·3 (C-2; doublet), 125·3 (C-5,6; doublet), 143·9 (C-7; doublet), 171·4 (C-4; singlet), 204·9 (C-1; singlet). Terrein in Ac_2O and pyridine gave the diacetate as a pale yellow viscous oil, mass spectrum, m/e 238 (M), 196 (M–CH_2CO), 135 (M–CH_2CO–Me CO_2H). CMR ($CDCl_3$): δ 19·5 (C-8), 20·5 and 20·8 (CH_3CO-, CH_3CO), 74·7 (C-3), 78·2 (C-2), 124·5 and 128·1 (C-5,6), 140·3 (C-7), 165·1 (C-4), 196·9 (C-1), 170·2 ($MeCO$, CH_3CO).

Mannitol and glycerides. Crushed, dried mycelium was extracted continuously with MeOH for 16 hr. After evaporation of the MeOH, residue was leached with 40–60° petrol to give a mixture of glycerides and a residue (A). The glycerides were refluxed with KOH in MeOH for 30 min to give free fatty acids which were methylated by brief treatment with CH_2N_2. The mixture of methyl esters was investigated before and after catalytic hydrogenation by GLC on a column (1·5 m × 3 mm) of celite coated with 10% EGSS-X at 200° and a N_2 flow of 45 ml/min. UV of the original glyceride mixture showed λ_{max}^{EtOH} 271 nm ($E_{1\,cm}^{1\%}$ = 8). Residue (A) was crystallized from EtOH to give mannitol, mp 165–166°; ν_{max}^{nujol} 3250 cm^{-1}; hexaacetate, mp 121–122°.

Acknowledgements—The authors thank the SRC and Shell Research Ltd., for financial support (AWD).

REFERENCES

1. Coats, J. H., Herr, M. E. and Herr, R. R. U.S. Patent, 3,585, 111.
2. Raistrick H. and Smith, G. (1935) *Biochem. J.* **29**, 606.
3. Misawa, M., Nara, T., Nakayama, K. and Kinochita, S. (1962), *Nippon Nogeikagaku Kaishi*, **36**, 699; (1965) C.A. **62**, 2213.
4. Qureshi, I. H., Kamal, A., Noorani, R., Aziz, S. and Husain, S. A. (1968) *Pak. J. Sci. Ind. Res.* **11**, 367.
5. Grove, J. F. (1954) *J. Chem. Soc.* 4693.
6. Clutterbuck, P. W., Raistrick, H. and Renter, F. (1937) *Biochem. J.* **31**, 987.
7. Barton, D. H. R. and Miller, E. (1955) *J. Chem. Soc.* 1028.
8. Auerbach, J. and Weinrab, S. M. (1974) *J. Chem. Soc., Chem. Somm.* 298.
9. Obtained from ARS Culture Collection Investigations, USDA.

Phytochemistry, 1975, Vol. 14, pp. 2082–2083. Pergamon Press. Printed in England.

3,6,8-TRIHYDROXY-1-METHYLXANTHONE—AN ANTIBACTERIAL METABOLITE FROM *PENICILLIUM PATULUM*

DOUGLAS BROADBENT, RICHARD P. MABELIS and HARRY SPENCER

Imperial Chemical Industries Ltd., Pharmaceuticals Division, Mereside, Alderley Park, Macclesfield, Chesire, SK10 4TG, England

(*Received* 19 *February* 1975)

Key Word Index—*Penicillium patulum*; fungus; norlichexanthone; 3,6,8-Trihydroxy-1-methylxanthone; biosynthesis; griseofulvin.

It is known that *Penicillium patulum* produces the antifungal antibiotic griseofulvin along with the biosynthetically related metabolites griseoxanthone C and griseophenones A, B and C.

We reinvestigated this organism because it was giving antibacterial activity and isolated griseofulvin, griseoxanthone C and griseophenone C along with 3,6,8-trihydroxy-1-methylxanthone, which was the only antibacterial metabolite (MIC vs *Clostridium welchii* = 25 ppm). It was identified from its UV and IR spectra, which were characteristic of other fungal xanthones [1]; its NMR spectrum (Ar–Me, 2 ArH as an Abqu J 2 Hz, 2 ArH as a multiplet, absence of O Me); and because on treatment with CH_2N_2 both it and griseoxanthone C were converted into the same product, 1-hydroxy-3,6-dimethoxy-8-methylxanthone (lichexanthone) [1].

3,6,8-Trihydroxy-1-methylxanthone occurs naturally as a metabolite of the lichen *Lecanora reuteri* and was given the trivial name norlichexanthone, [3a] and has been synthesized [3b].

Biosynthetically norlichexanthone would appear to be related to griseofulvin, the griseoxanthones and the griseophenones but it is the first such product in which all of the oxygen substituents occur as free phenolic hydroxyl groups. There are two ways to conceive of its formation.

One is the direct cyclization of 2-methyl-4,6,2′,4′,6′-pentahydroxybenzophenone which has been postulated as the first aromatic product in the biosynthesis of griseofulvin [4]. Alternatively, if, as has been suggested by Harris *et al.* [5], a polyketide precursor is methylated before it is cyclized into aromatic products, then it may be that norlichexanthone is formed by demethylation of griseoxanthone C.

EXPERIMENTAL

Production and isolation of the metabolites. A mutant strain of *Penicillium patulum* was grown on a glucose–corn-steep liquor medium under conditions specified in British Patent 784618. Filtered broth (600 l.) was acidified (pH 2) by the addition of mineral acid and extracted with EtOAc (1 × 200 l; 1 × 120 l). The EtOAc was evaporated to a thick, brown residue, part of which (188 g) was redissolved in MeOH (1:2 l) and evaporated onto Si gel (1 kg). This was packed as a dry column [6] on top of a further 1·5 kg of silica gel. The column was washed initially with toluene (5 l.), then $CHCl_3$ (20 l.) followed by $CHCl_3$–EtOAc (17:3) 4 l. and finally $CHCl_3$–EtOAc–EtOH (17:3:1) 10 l.

The first $CHCl_3$ fractions (6 l) were concentrated (200 ml) and the pptd crystals (5 g) identified as griseoxanthone C mp 253–255° (lit.[2] 253–255°); τ-3·5 and 0·2 (O<u>H</u>), 3·35 (AB *qu*, Ar<u>H</u>), 3·78 (AB *qu* Ar<u>H</u>), 6·2 (C<u>H</u>$_3$-O), 7·23 (C<u>H</u>$_3$-Ar). The mother liquors were diluted with EtOAc to a density < 1, washed with 2 N NaOH, and evaporated to yield griseofulvin, identified by direct comparison with a standard sample. The caustic washings were acidified (pH 5) and extracted with EtOAc. Evaporation of this extract gave an oil (32·8 g) which crystallized on standing. Recrystallization from toluene gave griseophenone C mp 175–178° (lit. [3] 183–185°); τ-1·2 (O<u>H</u>), 3·71 (2H, *s*, Ar<u>H</u>), 4·11 (2H, *s*, Ar<u>H</u>), 6·24 (OC<u>H</u>$_3$)., 6·34 (OC<u>H</u>$_3$), 7·90 (ArC<u>H</u>$_3$). Following these fractions the next 34 l. of eluate, on evapn, pptd norlichexanthone (42 g), which crystallized from aq Me_2CO mp 272–274° (lit. [7] 272–275°); blue-green with $FeCl_3$; positive Dimroth reaction [8]; *m/e* 258·0531; λ_{max}(EtOH), 241 nm (ε 36500), 311 nm (ε 22500); ν_{max} 3500, 3050, 1650, 1620, 1500, 830, 812, 760 cm^{-1}; τ-3·4 (O<u>H</u>) 3·4 (2H, *m*, Ar<u>H</u>), 3·85 (AB *q*, *J* 2Hz, Ar<u>H</u>), 7·24 (Ar–C<u>H</u>$_3$).

Methylation of norlichexanthone and griseoxanthone C. Methylation of both norlichexanthone and griseoxanthone C with diazomethane gave lichexanthone mp 185–187° (lit. 185–187°) [2].

Acknowledgements—We would like to thank Mr. Alan H. Davies for the fermentation and large scale extraction work.

REFERENCES

1. McMaster, W. J., Scott, A. I. and Trippett, S. (1960) *J. Chem. Soc.* 4628.
2. Rhodes, A., Boothroyd, B., McGonagle, P. and Somerfield, G. A. (1961) Biochem. J. **81,** 28.
3. Santesson, J. (1968) *Acta. Chem. Scand.* **22,** 1698; Santesson. J. and Sundholm, G. (1969) *Arkiv. Für Kem.* **30,** 426.
4. Scott, A. I. (1965) *Quart. Rev.* 19.
5. Harris, T. M., Howarth, T. Trefor and Carney, R. L. (1971) *J. Am. Chem. Soc.* **93,** 2511.
6. Loev, B. (1967) *Chem. Ind.* 2026.
7. Santesson, J. and Sundholm, G. (1969) *Arkiv. Für Kemi.* **30,** 427.
8. Dimroth, D. and Fanst, T. (1921) *Chem. Ber.* **54,** 3020.

Phytochemistry, 1975, Vol. 14, pp. 2083–2084. Pergamon Press. Printed in England.

LIPIDS AND PHENOLICS OF HEALTHY AND MALFORMED PANICLES OF *MANGIFERA INDICA**

MOHAN L. MAHESHWARI and SUNIL K. MUKERJEE

Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi-110012, India

(*Revised received* 17 *March* 1975)

Key Word Index—*Mangifera indica* L.; Anacardiaceae; healthy and malformed panicles; fats; sitosterol; phenolic acids; inositol; galactose.

Plant. Mangifera indica L (Var. Langra). *Uses.* Principal fruit crop of Indian subcontinent. Fruit is laxative, diuretic, diaphoretic, astringent and refrigerant, bark and kernel are astringent and tonic, leaves and dried flowers are useful in diarrhoea and chronic dysentry.

Previous work. Stembark [1], heartwood [1], leaves [1–3]. blossoms (essential oil [4], tannin [5], flavonoids [5] and ethyl gallate [6]), seed [7] and resin [8]. Malformation is a serious disease in *M. Indica* and a variety of reasons are ascribed [9,10]. This investigation was under-

* Contribution No. 79 from Division of Agricultural Chemicals, Indian Agricultural Research Institute.

† Percentage in malformed particles.