Phytochemistry, 1973, Vol. 12, pp. 1797 to 1798. Pergamon Press. Printed in England.

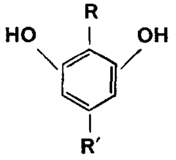
A NEW DIALKYLRESORCINOL FROM *STEMPHYLIUM MAJUSCULUM*

FRANK H. STODOLA, DAVID WEISLEDER and RONALD F. VESONDER
Northern Regional Research Laboratory, Agricultural Research Service, United States Department of Agriculture, Peoria, IL 61604, U.S.A.

(*Received* 24 *November* 1972. *Accepted* 10 *January* 1973)

Key Word Index—*Stemphylium majusculum*; Hyphomycetes; Fungi; resorcinol; stemphol.

METABOLIC products have been reported from only two species of *Stemphylium*, *S. radicinum*[1–4] and *S. sarcinaeforme*.[5] To extend our knowledge of this genus, we surveyed other species in this group and selected *S. majusculum* for detailed study when the mycelium of this organism yielded a new crystalline compound (stemphol) of m.p. 91°. This species was first described by Simmons in 1969.[6]



(I)

(Ia) R = $(CH_2)_3Me$; R′ = $(CH_2)_4Me$

(Ib) R = $(CH_2)_4Me$; R′ = $(CH_2)_3Me$

Elementary analyses and mass spectrometry gave $C_{15}H_{24}O_2$ as the molecular formula for stemphol. UV absorption and the phosphomolybdic acid test[7] showed the compound to be an alkylated resorcinol. NMR (two aromatic protons) indicated that two alkyl groups are present in stemphol. Four types of dialkylresorcinols are possible, but two of these can be eliminated since stemphol does not give a precipitate with $Hg(NO_3)_2$ and resorcinols with a free 2-position would be expected to give this test.[7,8] A vicinal arrangement of substituents is also unlikely, because compounds of this type would have only one easily replaceable ring hydrogen, and would not be expected to form a dibromo derivative with a mild reagent (N-bromosuccinimide), as does stemphol which thus must be I, confirmed by the two equivalent aromatic protons which appear in the NMR spectrum ($CDCl_3$) at

---

[1] CLARKE, D. D. and NORD, F. F. (1953) *Arch. Biochem. Biophys.* **45,** 469.

[2] GROVE, J. F. (1964) *J. Chem. Soc.* 3234.

[3] NOZOE, S., HIRAI, K., TSUDA, K., ISHIBASHI, K., SHIRASAKA, M. and GROVE, J. F. (1965) *Tetrahedron Letters* 4675.

[4] GROVE, J. F. (1971) *J. Chem. Soc.* 2261.

[5] SCOTT, P. M. and LAWRENCE, J. W. (1968) *Can. J. Microbiol.* **14,** 1015.

[6] SIMMONS, E. G. (1969) *Mycologia* **61,** 1.

[7] BUTENANDT, A. and STODOLA, F. H. (1939) *Ann. Chem.* **539,** 40.

[8] RASMUSSEN, M., RIDLEY, D. D., RITCHIE, E. and TAYLOR, W. C. (1968) *Australian J. Chem.* **21,** 2989.

δ6·18. From NMR (2 benzylic–CH_2–, 5 –CH_2– and 2 Me–) and MS [236–43 = 193 (β cleavage) and 236–56 = 180 (β cleavage plus rearrangement)], the side chains appear to be *n*-butyl and *n*-amyl; therefore, the structure of stemphol must be either (Ia) or (Ib). A related compound, 2-methyl-5-pentadecylresorcinol, has been isolated from cashew nutshell endosperm.[9]

EXPERIMENTAL

Production of stemphol. Stemphylium majusculum (NRRL 5269; ATTC 18520) was grown for 1 week at 28° on a potato-dextrose agar[10] slant. Pieces of the agar were floated on 1 l. of sterilized potato-dextrose medium[10] contained in a 2·8-l. Fernbach flask. After incubation for 45 days at 25° in still culture, the mycelium from eight flasks was separated and dried (33·4 g). Extraction with hot acetone gave 8·72 g of a brown semi-solid, which on SiO_2 column purification yielded 5·12 g of almost pure stemphol (m.p. 90–1°). The pure material (white needles from hexane) melted at 91–1·5°. (Found: C, 76·1; H, 10·38. $C_{15}H_{24}O_2$ requires: C, 76·23; H, 10·23) λ_{max} (95% EtOH) 273 nm (ϵ 1750) and 280 nm (ϵ 1630). ν_{max} (KRS-5 plate) 3270–3290, 2920, 2850, 1625, 1588, 1528, 1430, 1285, 1270, 1200, 1100, 990, 840, 725, 660 cm^{-1}. NMR δ ($CDCl_3$) at: 6·18 (*s*, 2, aromatic protons), 4·67 (*s*, 2, exchangeable OH protons), 2·48 (*q*, 4, two benzylic methylene quartets), 1·40 (*m*, 10), 0·90 (*m*, 6, two different methyl groups). The MS yielded prominent ions at *m/e* 236, 193 and 180. Stemphol gave positive Gibbs indophenol, Guareschi and diazo tests and negative $FeCl_3$, fluorescein and $Hg(NO_3)_2$ tests. In aq. alcohol stemphol shows no color with phosphomolybdic acid; when ammonia is added, a blue color appears. These tests were carried out according to the directions of Butenandt and Stodola.[7]

Stemphol diacetate. Acetylation (Ac_2O in pyridine) gave the diacetate as an oil, which crystallized at −20°. (Found: C, 71·2; H, 8·80. $C_{19}H_{28}O_4$ requires: C, 71·22; H, 8·81.) ν_{max} (NaCl disc) 2960, 2934, 2868, 1765 (phenol acetate), 1625, 1573, 1368, 1180–1210, 1100, 1022, 882 cm^{-1}. NMR δ ($CDCl_3$) at: 6·74 (*s*, 2, aromatic protons), 2·48 (*q*, 4, two benzylic methylene groups), 2·25 (*s*, 6, acetyl methyl protons), 1·40 (*m*, 10), 0·90 (*m*, 6, methyl protons).

Dibromostemphol. Stemphol (1 mmol) and *N*-bromosuccinimide (2 mmol) in 1 ml of CH_3CN for 1 hr at room temp. gave, after addition of H_2O, 394 mg of white crystals (m.p. 77–80°). Low-temperature crystallization from hexane yielded a pure dibromo compound in the form of white needles (m.p. 83–83·5°). (Found: C, 45·7; H, 5·51; Br. 40·2. $C_{15}H_{22}Br_2O_2$ requires: C, 45·71; H, 5·63; Br, 40·55.) ν_{max} (KRS-5 plate) 3510, 3410–3438, 2950, 2919, 2858, 1590, 1565, 1458, 1405, 1390, 1335, 1325, 1240, 1155, 1108, 1020, 725, 660 cm^{-1}. NMR ($CDCl_3$) at: 5·62 (*s*, 2, exchangeable OH protons), 2·78 (*q*, 4, two benzylic methylene groups), 1·40 (*m*, 10), 0·90 (*m*, 6, methyl protons).

---

[9] TYMAN, J. H. P. (1967) *Chem. Commun.* 982.

[10] HAYNES, W. C., WICKERHAM, L. J. and HESSELTINE, C. W. (1955) *Appl. Microbiol* **3**, 361.