

3-(ω -Phenylalkyl)catechols: Novel Phenolic Lipids Found in Sap of the Burmese Lac Tree, *Melanorrhoea usitate*

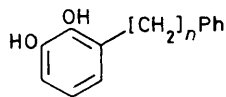
Yumin Du, Ryuichi Oshima,* Yoshio Yamauchi, and Ju Kumanotani

Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minatoku, Tokyo 106, Japan

Novel phenolic lipids, 3-(12-phenyldodecyl)catechol (**1**) and 3-(10-phenyldecyl)catechol (**2**) have been isolated from sap of the Burmese lac tree, *Melanorrhoea usitate*.

The sap of several kinds of lac tree has been used as excellent coating material in Asian countries for thousands of years.¹ The main constituent, thitsiol, of the sap of the Burmese lac tree, *Melanorrhoea usitate*, was characterized as a catechol with a C₁₇ n-alkyl or alkenyl side chain at position 4,^{2,3} but other constituents were not identified.

Applying a recently developed liquid chromatographic method,⁴ we succeeded in isolating 28 secondary plant metabolites from the sap of *Melanorrhoea usitate*, including thitsiol. Two novel phenolic lipids found in the sap have been identified as 3-(12-phenyldodecyl)- (**1**) and 3-(10-phenyldecyl)-catechol (**2**).

(1) $n = 12$ (2) $n = 10$

The native sap was mixed with 3 parts of acetone and was filtered to remove insoluble matter; the filtrate was evaporated and the residue fractionated by gel permeation chromatography ($2 \times$ TSK-gel G2000H₆, 2.2×60 cm; eluant, CHCl₃ at 5 ml/min; refractive index detection). The fraction (49.3 wt%) containing non-polymeric components was resolved by reversed-phase chromatography (TSK-gel LS410 5 m, 0.8×25 cm; eluant, MeCN-H₂O-AcOH, 80:20:2 v/v, at 2.5 ml/min; u.v. detection at 254 nm). This showed that the sap contained homologues of thitsiol (22 wt%), urushiol (4 wt%), laccol (6 wt%), 3-alkyl- or -alkenyl-phenols (2 wt%), 4-substituted catechol (1 wt%), and 5-substituted resorcinols (1 wt%) with an ω -phenylalkyl group, and (1) (53 wt%) and (2) (11 wt%).

Compounds (1), m.p. 65 °C, and (2) gave satisfactory elemental analyses, and possess phenyl and 3-substituted catechol groups which are linked by C₁₂ or C₁₀ methylene chains, as revealed by i.r. and ¹H (400 MHz) and ¹³C n.m.r. (25 MHz) data. In their electron impact mass spectra, the only prominent signals were the molecular ions [relative intensity, 94% for (1) and 100% for (2)], and ions at m/z 124 [100% for (1); 91% for (2)], 123 (97; 92), and 91 (56; 50). The m/z 123 and 124 ions arise from cleavage of the bond β to the catechol

ring, and McLafferty rearrangement of the catechol moiety of the molecular ion. The m/z 91 ion is a tropylium ion derived from the alkylbenzene residue.

Long-chain alkyl phenols are biosynthesized through the polyketide pathway;^{3,5} in certain cases, fatty acids are considered to be precursors of these compounds.⁶ The phenyl ring may arise from shikimate *via* a cinnamic acid intermediate, as in flavonoid biosynthesis.⁵ Compounds (1) and (2) are the first phenolic lipids which have a phenyl group in the side-chain, and consequently may be of mixed-precursor origin.

The authors thank The Southsea Association (Tokyo) and The Burmese Embassy in Tokyo for the supply of native sap, Dr. T. Miyakoshi for critical discussion, and Dr. K. Hatanaka for ¹³C n.m.r. measurements.

Received, 3rd December 1984; Com. 1693

References

- 1 J. Kumanotani, in 'Polymer Application of Renewable Resources Materials,' eds. C. E. Carraher and L. H. Sperling, Plenum, New York, 1983, p. 225.
- 2 R. Majima, *Chem. Ber.*, 1922, **55B**, 191.
- 3 J. H. P. Tyman, *Chem. Soc. Rev.*, 1979, 499.
- 4 Y. Du, R. Oshima, and J. Kumanotani, *J. Chromatogr.*, 1984, **284**, 463.
- 5 K. B. G. Torrsell, 'Natural Product Chemistry,' Wiley, Chichester, 1983.
- 6 A. J. Birch and F. W. Donovan, *Aust. J. Chem.*, 1953, **6**, 360.