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STRUCTURE OF PHELLODENDROSIDE

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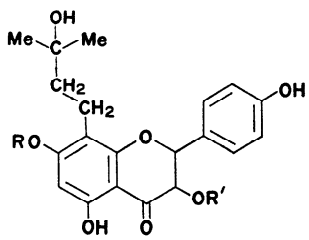
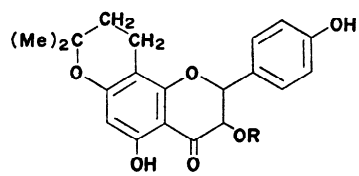
Key Word Index—*Phellodendron japonicum*; Rutaceae; phellodendroside; phellamuretin; flavanonol; isopentylflavanonol.

Abstract—The structure of phellodendroside is revised to (IV).

PHELLODENDROSIDE,[1] a previously unknown glycoside, noricariin,[2] and hyperoside[3] have been isolated from leaves of *Phellodendron japonicum* Maxim. Hydrolysis of phellodendroside gave phellamuretin (III) which has been obtained by hydrolysis of phellamurin (I). The structure of phellamuretin has been established by degradative and synthetical procedures.[4] Phellodendroside was previously given the structure (II); however the data now reported are inconsistent with this assignment.



(I) R = β-Glucosyl; R¹ = H
(II) R = H; R¹ = β-Glucosyl



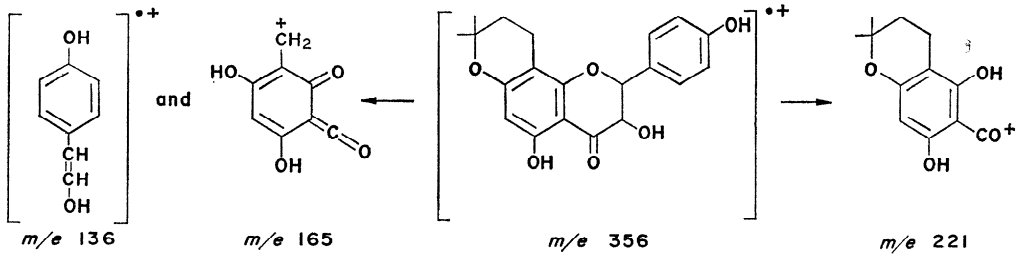
(III) R = H
(IV) R = β-Glucosyl

The UV spectrum of phellodendroside shows the long wavelength band at 294 nm and the position remains unchanged on addition of sodium acetate. This is strong evidence for the absence of a 7-OH group.[5] The NMR spectrum [$(CD_3)_2SO$] shows peaks for the aromatic protons, the 5- and 4′-OH protons but no peak for a 7-OH. Phenolic hydroxyls show characteristic resonances in dimethyl sulphoxide and the chemical shift depends on

[1] T. BODALSKI and E. LAMER, *Dissert. Pharm.* **15,** 319 (1963); *Acta Pol. Pharm.* **22,** 281 (1965).
[2] T. BODALSKI and E. LAMER, *Dissert. Pharm.* **21,** 181 (1969).
[3] T. BODALSKI and E. LAMER, *Dissert. Pharm.* **16,** 67 (1964).
[4] M. HASEGAWA and T. SHIRATO, *J. Am. Chem. Soc.* **75,** 5507 (1953); S. AKAI, *J. Pharm. Soc. Japan* **55,** 537 (1935); S. AKAI and T. MATSUKAWA, *ibid.* **55,** 705 (1935); S. AKAI and K. NAKAZAWA, *ibid.* **55,** 719 (1935).
[5] T. J. MABRY, in *Perspectives in Phytochemistry* (edited by J. B. HARBORNE and T. SWAIN), Academic Press, London (1969).

the ring substitution pattern.[6] Sometimes the resonance is absent due to rapid exchange of the proton with extraneous water but, as would be expected, when this occurs in the flavanoid series both 7- and 4'-OH resonances are removed.[7] Thus from the UV and NMR data we conclude that phellodendroside has no free 7-OH and must therefore be represented by structure (IV). The two methyl groups of phellodendroside are magnetically non-equivalent They appear at differing τ values which remain unchanged at frequencies of 60 and 100 MHz although the separation in Hz between the resonances changes with frequency. The separation remained unaltered on the addition of deuterium oxide.

The MS of phellodendroside shows the highest mass peak at *m/e* 356 corresponding to fragmentation to the aglucone (III). The further fragments can be rationalised as shown. The MS supports our structure for phellodendroside but it is not conclusive evidence for the cyclised C_5 side chain since ring closure could occur in the spectrometer inlet system.



EXPERIMENTAL

Phellodendroside was extracted from *Phellodendron japonicum* Maxim. UV (MeOH), λ_{max} 232 nm, log ϵ 4·24 and 294 nm, log ϵ 4·18, after addition of sodium acetate λ_{max} 295 nm, log ϵ 4·16. NMR τ [$(CD_3)_2SO$] – 1·8 (1H, 5-OH), 0·43 (1H, 4'-OH), 2·68 (*d*, 2H, 2',6'-H), 3·20 (*d*, 2H, 3',5'-H), 3·69 (*s*, 1H), 4·0–5·6 (multiplets), 8·42 (3H, Me), 8·49 (3H, Me). MS (direct insertion) *m/e* 356 (43%), 327 (14), 221 (55), 165 (100), 136 (30), 134 (73), 107 (73).

[6] M. T. TRIBBLE and J. G. TRAYRAHAM, *J. Am. Chem. Soc.* **17**, 428 (1964).
[7] T. J. BATTERHAM and R. J. HIGHET, *Austral. J. Chem.* **17**, 428 (1964).