Tecleaverdoornine: a New *C*-Prenylated Phenylated Furoquinoline

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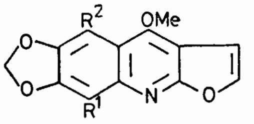
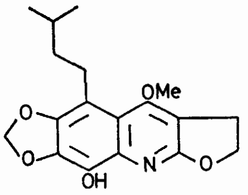
Summary The structure of the new furoquinoline, tecleaverdoornine is deduced from its spectra and chemical reactions.

IN continuation of our work on West African medicinal plants of the plant family Rutaceae we have examined chemically the extracts of the stem bark of *Teclea verdoorniana* (*T. grandifolia*)[1] collected from Nkolbisong near Yaounde, Cameroon and have isolated what, to our knowledge, is the first naturally occurring furoquinoline with ring A fully substituted which also belongs to the class of rare[2] naturally occurring phenolic furoquinolines. The combined hexane and chloroform extracts of the milled stem bark of *T. verdoorniana* on fractionation by column chromatography gave lupeol[3] (1%), m.p. 212 °C; flindersiamine[4] (**1**) (0·15%), m.p. 208 °C; kokusaginine[5] (0·003%), m.p. 168 °C; and four furoquinoline alkaloids including tecleaverdoornine† (0·003%) m.p. 191 °C, which are considered to be new. The evidence leading to structure (**2**) proposed for tecleaverdoornine is described here.

Tecleaverdoornine, $C_{18}H_{17}O_5N$, m.p. 191 °C (from acetone), has ν_{max} (KBr) 3410 (OH), 3154, 3130, 1680, 1610, and 1535 cm^{-1} and a number of strong absorptions in the region 1200—700 cm^{-1} (unsaturation and aromaticity); λ_{max} ($CHCl_3$) 248 (ϵ 28,000), 263 (ϵ 58,100), 330 (ϵ 10,000), and 350 nm (ϵ 6,500); ^1H n.m.r. δ ($CDCl_3$ + Me_4Si) 1·7 (3H, s, Me), 1·8 (3H, s, Me), 3·8 (2H, crude d, *J* 7 Hz, $ArCH_2$), 4·35 (3H, s, OMe), 5·3 (1H, m, $ArCH_2$–C*H*=), 6·1 (2H, s, $-OCH_2O-$), 7·1 (1H, d, *J* 2 Hz, β-furan H), and 7·55 (1H, d, *J* 2 Hz, α-furan H); *m/e* 327 (M^+), 312, 296, 284, 282, 270, 254, 147, 141, 131, 119, 69, and 41. It gave a positive Labat's test[6] for the $-OCH_2O-$ group and a deep green solution in methanol with ferric chloride indicating a phenolic group. The spectra were in several ways



(1) R^1 = OMe, R^2 = H
(2) R^1 = OH, R^2 = $CH_2CH{=}CMe_2$
(3) R^1 = OMe, R^2 = $CH_2CH{=}CMe_2$
(4) R^1 = OCOMe, R^2 = $CH_2CH{=}CMe_2$



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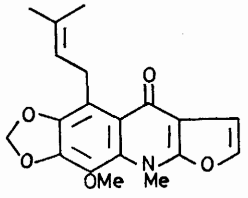

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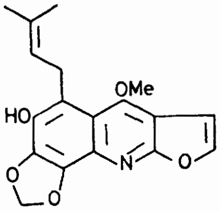

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† All new compounds gave satisfactory microanalyses.

similar to those of (**1**). Tecleaverdoornine formed a methyl ether (**3**), m.p. 139—140 °C, on treatment with ethereal diazomethane, an acetate (**4**), m.p. 212 °C, on treatment with acetic anhydride in pyridine, and a tetrahydro derivative (**5**), m.p. 152—153 °C, on hydrogenation in ethyl acetate in the presence of 10% Pd–C. The methyl ether ($C_{19}H_{19}NO_5$) and the acetate ($C_{20}H_{19}NO_6$) showed no hydroxy absorption in their i.r. spectra. The ^1H n.m.r. spectrum of (**3**), had an additional methoxy absorption at δ 4·20 which compares well with the chemical shift (δ 4·27) observed[7] for the 8-OMe group of (**1**), while the ^1H n.m.r. spectrum of (**4**) showed an enol acetate absorption at δ 2·5.

The mass spectra of (**2**) and (**3**) gave fragment ion peaks which were in agreement[8] with their structural relationship with (**1**). Peaks corresponding to the $M-1$, $M-15$, $M-43$, and $M-73$ fragment ions were observed in the spectrum of (**2**) while that of (**3**) had peaks corresponding to the fragment ions $M-1$, $M-15$, $M-29$, $M-69$, and $M-71$. The peak at m/e 69 in the spectra of both compounds was assigned to the isopentenylium ion formed from the isoprenyl side chain.

The low field chemical shift (δ 3·8) of the benzylic hydrogens of the isoprenyl side chain at C-5 is probably due to the peri-effect of the C-4 methoxy group. The substitution pattern in (**2**) was supported by the fact that in the ^1H n.m.r. spectrum of isotecleaverdoornine methyl ether (**6**), m.p. 170 °C (prepared by the action[9] of MeI on tecleaverdoornine methyl ether), the benzylic hydrogens absorbed at δ 4·10 demonstrating the stronger peri-effect of the carbonyl at C–4 in (**6**). That tecleaverdoornine failed to yield a chroman on treatment with acid eliminated alternative structural proposals such as (**7**).

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