titatively estimated by measuring A at their respective λ_{max}. Identifications were based on R_fs, colour in visible light, colour in UV light and λ_{max}. Two anthocyanidins, cyanidin (R_fs 0.22 in formic, 0.49 in Forestal. λ_{max} 535 nm) and pelargonidin (R_fs 0.33 in formic and 0.68 in Forestal, λ_{max} 520), were identified in red-leafy bracts and red-green leaves. Total chlorophyll, Chl.a and Chl.b were quantitatively extracted and estimated spectrophotometrically [4–6]. Chloroplast isolation and Hill activity measurements are based on an earlier method developed in our laboratory [7, 8].

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A NEW QUINOLINE ALKALOID FROM *RUTA GRAVEOLENS**

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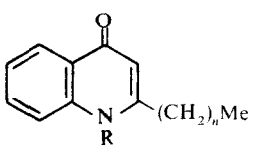
Key Word Index—*Ruta graveolens*; Rutaceae; quinoline alkaloids; 1-methyl-2-*n*-nonyl-4-quinolone.

4-Quinolones containing long alkyl chains in the 2-position (pseudans) were first obtained from micro-organisms, but in recent years pseudans have also been isolated from rutaceous species. The 2-alkyl-1-methyl-4-quinolones (**1**; R = Me, n = 10, 12 or 14), for example, were shown to be constituents of *Evodia rutaecarpa* [1], whereas the 4-quinolones (**1**; R = H, n = 10–13) lacking an *N*-methyl group were obtained as an unresolved mixture from the roots of *Ruta graveolens* [2]. We now report the isolation of a new alkaloid, 1-methyl-2-*n*-nonyl-4-quinolone (**2**) from the aerial parts of *Ruta graveolens*.

Extraction of the leaves, shoots and flowers of *R. graveolens* and chromatography of the acid-soluble portion resulted in the identification of the furoquinoline alkaloids dictamnine, γ-fagarine, kokusaginine and skimmianine, which have been isolated previously from the plant [3]. The more polar fraction contained the 2-aryl-*N*-methyl-4-quinolone, graveoline, also a known constituent [4].

A new alkaloid, 1-methyl-2-*n*-nonyl-4-quinolone (**2**), was shown to be a minor component of the graveoline fraction, and its structure was established by spectroscopy. The UV spectrum in neutral and in acid solution was consistent with that of a 4-quinolone unsubstituted in the homocyclic ring; this was confirmed by IR absorption at 1618 cm^{-1} (4-quinolone carbonyl) and by the ^1H NMR resonance at δ 8.45, characteristic of an aromatic proton at C-5 deshielded by a 4-quinolone carbonyl group (cf. graveoline). The ^1H NMR spectrum also confirmed the presence of an *N*-methyl group, a proton at C-3 and an alkyl chain at C-2. Although elemental analysis and the mass of the molecular ion formed in the mass spectrometer showed that the alkaloid contained a C_9H_{19} substituent, the complete structure of

* Part 18 in the series "Quinoline Alkaloids". For Part 17 see Grundon, M. F. and James, K. J. (1979) *J. Chem. Soc. Perkin Trans.* 1 (in press).



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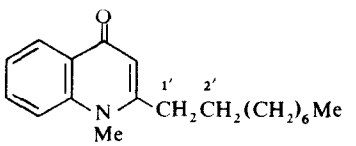

2

this group was only established by a more detailed analysis of the mass spectrum. Thus, the base peak at *m/e* 173 is clearly due to rearrangement of the molecular ion involving cleavage of the C-1′–C-2′ bond, as in the case of dihydroevocarpine (1; R = Me, n = 12), and the stepwise loss of C_1 units in regular progression is typical of an *n*-alkyl group [1, 5].

EXPERIMENTAL

The ^{1}H NMR spectra were determined with a Perkin–Elmer R12 spectrometer using TMS as internal standard, and MS with an A.E.I. MS 902 instrument.

Dried leaves, shoots and flowers of *Ruta graveolens* (1.69 kg) were extracted with EtOAc and the soln was extracted with 2N HCl. Basification of the acid extract with Na_2CO_3 and extraction with $CHCl_3$ gave the tertiary base fraction (2.4 g), which was chromatographed on alumina. After removing small quantities of coumarins by elution with C_6H_6, elution with Et_2O and PLC on Si gel with $CHCl_3$ gave dictamnine in prisms (from petrol (bp 40–60°)), mp 127–130°, identical (mmp and ^{1}H NMR) with an authentic sample. Elution with Et_2O–$CHCl_3$ (4:1) afforded a mixture of alkaloids (620 mg) and PLC on Si gel with C_6H_5Me–EtOAc–HCO_2H (5:10:2) gave γ-fagarine, mp 140° (lit. [6], mp 142°) (prisms from Et_2O), kokusaginine, mp 167–170° (lit. [7], mp 168–169°) (prisms from EtOH) and skimmianine, mp 176–178° (lit. [7], mp 177°). Elution with $CHCl_3$ furnished a mixture of alkaloids (440 mg) and PLC on Si gel with C_6H_5Me–EtOAc–HCO_2H (5:6:2) gave graveoline, separating from Et_2O–$CHCl_3$ in plates (120 mg), mp 186–188° (lit. [8], mp 186–187°): R_f 0.41; ν_{max}^{KBr} cm^{-1}: 1617; ^{1}H NMR (60 MHz, $CDCl_3$); δ 3.65 (3H, *s*, NMe), 6.09 (2H, *s*, $OC\underline{H}_2O$), 6.22 (1H, *s*, C-3) and 8.45 (1H, *d*, C-5); MS *m/e* (rel. int): 279 [M$^+$] (82), 251 [M − CO] (100) and 207 (70) and 1-methyl-2-*n*-nonyl-4-quinolone (2), (plates from C_6H_6–C_6H_{14}) (25 mg), mp 71–75°, R_f 0.14 (Si gel with $CHCl_3$). ν_{max}^{KBr} cm^{-1}: 1618; λ_{max}^{MeOH} nm: 335 (ε 15 500), 323 (ε 15 330) and 236; $\lambda_{max}^{MeOH-HCl}$ 301 and 233; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.1–1.8 (*m*, $ArCH_2$ $(C\underline{H}_2)_7C\underline{H}_3$), 2.71 (2H, *m*, $ArC\underline{H}_2CH_2$-), 3.72 (3H, *s*, NMe), 6.22 (1H, *s*, C-3), 7.35–7.60 (3H, *m*, C-6, C-7 and C-8) and 8.45 (1H, *d*, J = 8 Hz, C-5); MS *m/e* (rel. int.): 285.1916 ($C_{19}H_{27}NO$ requires 285.2094) [M$^+$] (31), 270 [M − Me] (3), 256 [M − C_2H_5] (4), 242 [M − C_3H_7] (5), 228 [M − C_4H_9] (7), 214 [M − C_5H_{11}] (2), 200 [M − C_6H_{13}] (8), 186 [M − C_7H_{15}] (49) and 173 [M − C_8H_{16}] (100). (Found: C, 80.0; H, 9.5; N, 4.8. $C_{19}H_{27}NO$ requires: C, 80.0; H, 9.5; N, 4.9%).

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