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SHORT COMMUNICATIONS

DISTRIBUTION OF BENZOQUINONE PIGMENTS IN KENYAN MYRSINACEAE

J. Ogweno Midiwo*, L. Manguro Arot and C. Lumumba Mbakaya
Chemistry Department, College of Biological and Physical Sciences,
University of Nairobi, P.O. Box 30197, Nairobi, Kenya

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ABSTRACT. The distribution of benzoquinones in Kenyan Myrsinaceae is such that the three in *Maesa* are different from those in the three other genera *(Myrsine, Rapanea, Embelia)* which contain the same two benzoquinones. The two chemical groups are in accord with the morphological classification of these plants.

INTRODUCTION

The family Myrsinaceae is represented in Kenya by four species in four different genera - *Maesa lanceolata* Forsk, *Myrsine africana* L., *Rapanea melanphloes* (L). Mez. and *Embelia schimperi* Vatke (1). The species all find ethnopharmacological application as anthelimintics (2). Watt and Breyer-Brandwijk (3) claimed that embelin occured in *Maesa lanceolata* and was the only benzoquinone in the other three species. However eleven Myrsinaceae from Japan have since been studied and these show the presence of embelin and/or rapanone, maesaquinone, acetylmaesaquinone and other related quinones (4). In 1983 *M. lanceolata* from Kenya was reported to contain a host defence stimulant, maesanin (5). We embarked on a comprehensive chemical study of the local Myrsinaceae and have observed chemical relationship of plants within the group which correlates with the morphological classification (1).

RESULTS AND DISCUSSION

The results are listed on Table 1. There is a clear discontinuity in the distribution of quinones such that the benzoquinones with C_{15} to C_{19} side chains are restricted to *Maesa* while benzoquinones with shorter side chains (C_{11}-C_{13}) are found in *Myrsine, Rapanea* and *Embelia*. These compounds are therefore of taxonomic significance.

EXPERIMENTAL

Instruments. Melting points were determined using Gallenkamp melting point apparatus. The UV/VIS spectra were obtained using DU-50 spectrophotometer. The IR spectra were recorded as KBr pellets on a Perkin-Elmer Infrared 720 instrument. The ^1H NMR spectra were taken on a Varian 200 MHz spectrometer

Table 1. Benzoquinone pigments in Kenyan Myrsinaceae (g/kg)

	Embelin/ rapanone	Macrophyllin	Maesaquinone	Acetylmaesaquinone	Maesanin
Maesa lanceolata					
Fruits	-	-	110.1	5.0	0.41
Root bark	-	-	26.93	5.1	0.65
Stem bark	-	-	21.5	0.42	0.01
Leaves	-	-	13.5	0.45	0.21
Myrsine africana					
Fruits	41.0	0.2	-	-	-
Root bark	13.1	0.1	-	-	-
Stem bark	14.33	0.12	-	-	-
Leaves	18.2	0.01	-	-	-
Rapanea melanphloes					
Fruits	94.7	0.032	-	-	-
Root bark	72.7	0.17	-	-	-
Stem bark	26.3	0.18	-	-	-
Leaves	25.0	0.09	-	-	-
Embelia schimperi					
Fruits	43.1	0.1	-	-	-
Root bark	10.1	0.07	-	-	-
Stem bark	11.2	0.08	-	-	-
Leaves	10.7	0.01	-	-	-

while the MS were obtained on a Masslab VG.

Plant materials. The plants were collected from different parts of Kenya and authenticated at the Kenya National Herbarium, Nairobi, where voucher specimens are deposited: *E. schimperi* Vatke, was collected from Ngong Hills, at an altitude of 2400 m; *M. lanceolata* Forsk, was obtained from both Naru Moro (on the slopes of Mt. Kenya) at 2000 m and at Kakamega forest; *R. melanphloes* (L), Mez was obtained from the moorland of the Aberdare range at 3400 m. The parts of the plants collected were usually ground into a fine powder before solvent extraction.

Solvent extraction. Each plant part (150-200 g) was extracted continuously in a soxhlet apparatus using chlorform for 24 hr. The solvent was then removed from the extract in a rotary evaporator.

Chromatography. Analytical tlc was performed using silica gel plates impregnated with 3% oxalic acid solution and eluted with n-hexane/ethyl acetate/acetic acid (17:2:1). With this solvent system, the components had the following R_f values maesaquinone 0.6; acetylmaesaquinone 0.5; maesanin 0.2; embelin/rapanone 0.4; macrophyllin 0.3. Column chromatography was performed on 6N HCl washed silica gel with the solvents, n-hexane, n-hexane/benzene (4:1) and chloroform. These usually gave homogenous fractions of the following products.

Maesaquinone. M.p. 122-124° from methanol, lit (4) 123°C; UV λ_{max} (MeOH) 440 nm (log ε, 2.40), 294 nm (4.40); ^{1}H NMR $(CDCl)_3$ δ 7.59 (s, 2H), 5.38 (m, 2H), 2.40 (t, 2H), 2.0 (m, 4H), 1.94 (s, 3H), 1.26 (m, 26H), 0.9 (t, 3H); IR ν_{max} 1620 cm^{-1} (C=0); MS, m/z (rel. int.): 418 (M$^+$, 35), 390 (17), 364 (17), 169 (65), 168 (100), 156 (13), 139 (23).

Acetylmaesaquinone. M.p. 30-35°C from MeOH lit. (4) 28-34°C;UV λ_{max} (MeOH) 410 nm (log ε, 2.85) and 275 (4.20); ^{1}H NMR $(CDCl_3)$ δ 7.05 (s, 1H) 5.38 (m, 2H), 2.40 (t, 2H), 2.25 (s, 3H);IR ν_{max} 1780 and 1680 (C=0); MS, m/z (rel. int.)

460 (M^+, 12), 418 (13), 363 (100), 362 (27), 169 (38), 168 (38), 156 (18), 139 (9), 69 (14).

Maesanin. M.p. 67-68° from MeOH lit. (5) 69-73°C; UV λ_{max} (MeOH) 420 nm (log ε 2.7), 280 (4.2); ^{1}H NMR ($CDCl_3$) δ 7.21 (s, 1H), 5.94 (s, 1H), 5.35 (m, 2H), 3.85 (s, 3H), 2.40 (t, 2H), 2.0 (m, 4H), 1.26 (m, 18H), and 0.87 (t, 3H); IR ν_{max} 1650 and 1610 cm^{-1}; MS, m/z (rel. int.) 362 (M^+ 60), 169 (12), 168 (100), 167 (30), 156 (14), 153 (12), 125 (8.9).

Embelin/rapanone mixture. M.p. 140-143° from MeOH lit. (4) 141-142°C; MS, m/z (M^+ 294 and 322).

Macrophyllin. M.p. 66-68° from MeOH, lit. (6) 65-67°C; UV λ_{max} (MeOH) 420 nm (log ε, 2.80), 289 (4.50); ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 2H), 2.45 (t, 4H), 1.83 (s, 6H), 1.5 (m, 4H), 1.25 (m, 32H) and 0.88 (t, 6H); IR ν_{max} 1620 cm^{-1} (C=0); MS, m/z (rel. int.) 582 (M^+ 3), 294 (3), 179 (16), 155 (12), 142 (8), 43 (100).

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