Bull.Chem.Soc.Ethiop. **1993**,7(1) 67-69.

BIEMBELIN - A NEW SYMMETRICAL BISBENZOQUINONE FROM *RAPANEA MELANPHLOES*

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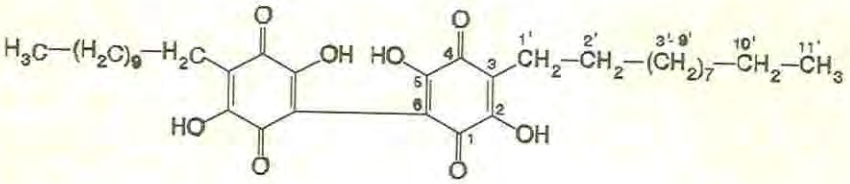
(Received November 27, 1991; Revised March 10, 1993)

ABSTRACT. A minor orange pigment metabolite in the fruits of *R. melanphloes* is 6,6"-bis-(2,5-dihydroxy-4-undecyl-3,6-benzoquinone) or 6,6'-biembelin.

INTRODUCTION

The Myrsinaceae are a highland family of plants which are very rich in benzoquinones. These quinones may have one or two quinonoid rings with or without additional long chain alkyl or alkenyl side chains [1-4]. In our continued analysis of Kenyan indigenous Myrsinaceae we have now examined *Rapanea melanphloes* (L), Mez and isolated a bisbenzoquinone, 6,6"-bis-(2,5-dihydroxy-3-undecyl-1,4-benzoquinone) or 6,6'-biembelin (**1**).



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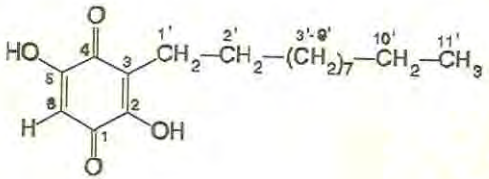

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RESULTS AND DISCUSSION

6,6'-Biembelin (**1**) is an orange pigment which turns purple on exposure to ammonia either on TLC or in a test-tube suggesting it to be a hydroxylated benzoquinone. The UV-Vis spectrum has peaks at 420 and 280 nm which are typical of a dihydroxylated benzoquinone like embelin (**2**) [5]. Even though, the molecular weight is 586, both ^{1}H and ^{13}C NMR spectra are devoid of complexities indicating the symmetrical nature of the compound. The ^{1}H NMR spectrum of **1** is largely similar to that of embelin, however, the ^{13}C NMR spectrum is markedly different in that signals are observed for each of the ring carbons (Table 1).

Table 1. ^{13}C and (^{1}H) NMR chemical shifts (δ, ppm) of 6,6'-biembelin (**1**) and embelin (**2**).

Position	2	1
1	-	120.0
2	-	150.0[b]
3	117	182.1[a]
4	-	116.7
5	-	149.6[b]
6	102.2 (6.05,*s*)	176.8[a]
1'	31.9 (2.45,*t*)	31.6 (2.46,*t*)
2'	28.5 (1.45,*m*)	27.5 (1.50,*m*)
3'-9'	29.5 (1.30,*m*)	29.0 (1.30,*m*)
10'	22.5 (1.24,*m*)	22.5 (1.24,*m*)
11'	14.1 (0.88,*t*)	14.0. (0.88,*t*)

[a,b]Chemical shifts may be interchanged.

The ^{13}C NMR spectrum of embelin (**2**) (Table 1) in $CDCl_3$ at ambient temperatures shows only two peaks for the ring carbons assigned to C-3 and C-6. This has been attributed to the fluxional nature of 2,5-dihydroxybenzoquinone systems [6]. Such tautomerism was not observed in 5-*O*-methylembelin since in this case signals corresponding to each of the carbons are observed. On the other hand the carbon chemical shifts of the alkyl side chain are identical to those of **2**. The IR spectrum shows only one carbonyl band at 1620 cm^{-1} again stressing symmetry. 6,6'-Biembelin is therefore a bisbenzoquinone which can be considered to arise from embelin or a precursor by oxidative coupling and has been assigned structure **1**. Its existence in *R. melanphloes* fruit is not surprising since embelin exists up to a level of 10% in this organ [1].

EXPERIMENTAL

Instruments. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The UV-Vis spectra were obtained with a DU-50 spectrophotometer while the IR spectra were recorded as KBr pellets on a Perkin-Elmer 720 instrument. The MS were determined on a JEOL JMS-D300 mass

spectrometer and ^{1}H and ^{13}C NMR spectra were acquired using a JEOL GSX-400 instrument with tetramethylsilane as internal standard.

Plant material. R. melanphloes was collected from Kithembe Hills in Machakos district of Kenya's Eastern province and a voucher specimen (No. 89/4) is deposited at the University of Nairobi Botany Department Herbarium.

Isolation and characterisation of 1. The fruit powder (125 g) was defatted with 2000 ml cold hexane and then extracted with 2000 ml cold dichloromethane. Removal of the dichloromethane gave a dark brown solid (16.3 g) which was applied on a silica gel column treated with 3% oxalic acid solution and eluted with n-hexane-dichloromethane mixtures.

Fractions which eluted with 1:2 n-hexane-dichloromethane afforded compound **1** (25 mg, 0.02%).

6,6'-Biembelin (**1**) R_f 0.41 (n-hexane: ethyl acetate: acetic acid,15:4:1); M.P. 135-137°; UV-Vis $\lambda_{max}^{\cdot}$ (MeOH) nm (logε): 420 (2.76), 280 (4.51); IR ν_{max} (KBr) cm^{-1}: 3250, 1620 (chelated C=O stretch); MS m/z (rel. int.): 586 M^+ (9.0), 153 (49), 97 (14), 69 (20), 57 (24), 44 (100). HRMS 586.2684 (calc. for $C_{34}H_{50}O_8$ = 586.3507).

ACKNOWLEDGEMENTS

JOM thanks the Matsumae International Foundation for fellowship and Professor S. Natori of Meiji College, Tokyo for additional financial support. S. Natori and colleagues are also thanked for useful discussions. The University of Nairobi is acknowledged for research grant.

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