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Lignans from the Commercial Timber *Hallea Ciliata P.* Commonly Called Abura

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Abstract

Examination of the heart wood powder of the important commercial timber Hallea ciliate P. commonly called Abura of the family Rubiaceae, usually found in fresh water swamp in the rain/tropical forest of Delta State of Nigeria was done by soxhlet extraction using n-hexane and ethanol. Flash column chromatography of the ethanol crude product eluted with ethyl acetate gave mainly one product (7) mpt. 152-154 °C in 0.70% yield. Though the mass spectrum fragment ions at m/e 164, 149, 135 and 121 suggest that the product(7) has the arboreol (3) frame work, the absence of the peak at m/e 338 which is characteristic of arboreol and the base peak at m/e 151 show that compound (7) is not arboreol. This is confirmed by the failure of (7) to cleave with sodium periodate. The proton magnetic resonance spectrum with protons signals at δ4.06 and 4.96 table 2 confirms a simple symmetrical structure identified as 1,5 – dihydroxy- 2,6 – bis methylene dioxy phenyl – 3,7-dioxobicyclo [3,3,0] octane.

1. Introduction

The substituted furofurans which are derivatives of 3,7-dioxobicyclo [3,3,0] octanes (1) are about the largest of the five classes of lignans known (Jack, 2002). They are defined as phenyl propanoid dimmers that are often isolated from different parts of plants found mostly in the rain and tropical forests. They are formed biogenetically by an oxidative coupling of appropriate cinnamyl alcohols present in plants using their enzymes. Amongst them are some novel hydroxy compounds like gmelinol (2), arboreol (3), its 2-O-methyl ether (4) and 2-O-ethyl ether (5) that were isolated from the heart wood of the Indian specie *Gmelina arborea* (Anjaneyulu et al, 1977). Recently, our extraction of the bark of *Gmelina arborea* obtained from the University of Science and Technology Port Harcourt resulted in the isolation of a 2,6 – diaryl substituted dilactone (6) (Jack and Orubite, 2009].

We have now examined the heart wood powder of another timber *Halleaciliata. P*commonly called Abura of the family Rubiaceae usually found in fresh water swamp in the rain/tropical forest of Delta state in Nigeria for its constituents and obtained mixture of products from which a major constituent named 1,5-dihydroxy-2,6-bis-methylenedioxyphenyl-3,7-dioxobicyclo [3,3,0] octane (7) was characterised by its spectral data such as infra-red ^{1}H, ^{13}C n.m.r. and mass spectra.

2. Materials and Methods

Melting point (uncorrected) was determined on a Koffler block apparatus. Infra-red spectrum was recorded on Perkin Elmer 237 Spectrophotometer. Mass spectrum was obtained on an AET MS 9 double focussing instrument at 250 ^{o}C and 70eV. ^{1}H and ^{13}C decoupled n.m.r. spectra were run in $CDCl_3$ from Varian HA100 and XL 100 spectrophotometers respectively using TMS as an internal standard and chemical shifts are given as δ (ppm). Thin layer chromatography (TLC) was run on silica gel GF 254 plates using toluene-ethylacetate 5:1 as solvent.

The heartwood of *Hallea ciliata* obtained from Burutu in Delta State was chopped into little strips, sundried and ground into a powder. 300g of the powder was successively extracted in a soxhlet extractor with n-hexane for 4hrs and then with ethanol for another 4hrs. The light yellow n-hexane extract 1.2l was distilled off leaving 2g residue which did not crystallise overnight but showed several overlapping spots on tlc plate and so was not studied further. The light brown ethanol extract (1litre) was concentrated to give 4.0g residue which was adsorbed upon silica gel and placed on a flash column of silica gel and eluted with Toluene-ethyl acetate 5:1 v/v. On work up of the eluent, 2.40g of solid was obtained which crystallised in ethyl acetate to give 2.20g of colourless solid mpt. 152-154^{o}C. Yield 2.20g (0.70Th)

IR (KBr)(OH) 3540 – 3450; (CH) 3020 – 2920, (arom.) 1604cm^{-1} .

^{1}H n.m.r ($CDCl_3$) OH, 2.45b.s; H – 4/8, 4.06s; H – 2/6, 4.96s; OCH $_2$O, 5.93s; arom., 6.90 – 6.70 m.

^{13}C n.m.r. ($CDCl_3$) C – 4/8, 76.43; C – 2/6, 86.86; C – 1/5 87.51; C – 1^{I}/1^{II}, 129.52; C – 3^{I}/3^{II} and C – 4^{I}/4^{II}, 147 .91; C – 2^{I}/2^{II}, 107.47; C-5^{I}/5^{II}, 108.30; C – 6^{I}/ 6^{II}, 120.22, OCH_2O, 101.42.

Found C, 5.27; H, 4.76% $C_{20}H_{18}O_8$ requires C, 5.18; H, 4.66%.

3. Results and Discussions

Compound (7) obtained in 0.70% yield has a melting point of 152-154^{o}C. It has bands at 3540-3450cm^{-1} and 1604cm^{-1} corresponding to (OH) and aromatic groups respectively in the infra red spectrum.

It gave a molecular ion M$^+$at m/e 386 (30.6) accurately mass measured to correspond to a molecular formula of $C_{20}H_{18}O_8$which is isomeric with arboreol (3) in the mass spectrum. This fragmented to give other fragment ions at m/e 121, 135 and 149 (see fig.2) characteristic of the presence of methylene dioxyphenyl substituent and also confirmed by the positive Labat's test (Anjaneyulu*et al*, 1975, Jack*et al*, 2006).An ion at m/e 338 characteristic of arboreol is not significant (0.4) in compound (7). However, many other ions corresponding to those observed in the spectra of other substituted furofurans like sesamin (1) and arboreol (3) are also present. In particular, abundant ions at m/e 177 and m/e 164 due to vertical and horizontal cleavages respectively of the bicyclo [3,3,0] octane lignan skeleton are evidenced (see table 1). Whereas the base peak in arboreal is 149, in compound (7) it is 151.

The proton magnetic resonance spectrum gave a remarkably simple spectrum for a symmetrical structure. (Table 2). For instance, the usual high field signals at δ3.30-δ3.15 due to the methine protons H-1 and H-5 which are characteristic of the furofurans(1)were absent. This suggests that the H-1 and H-5 protons are occupied by another group i.e the hydroxygroups which appeared at δ2.45 as broad singlet. On shaking with D_2O however, this signal disappeared. The fact of the appearance of the benzylic protons H-2 and H-6 as singlet shows that they are not coupled to the methine protons H-1 and H-5. In other furofurans (1), the benzylic H-2 and H-6 protons always appear as doublet with coupling constant of 4Hz in the region of δ4.68- δ 4.70whereas in compound (7) they appeared as singlet and shifted to δ4.96 by the OH groups atH-1 and H-5. Similarly, the H-4 and H-8 methylene protons which usually appear as double doubletor multiplet around δ3.70 in (1) are moved to δ4.06 as singlet in compound (7) by the hydroxyl groups. The ^{1}H n.m.r pattern of compound (7) and its failure to cleave with sodium peroidate corroborates evidence that compound (7) is not a 1,2-diol as arboreal(3) but a 1,5-diol.

The coincidence of the signals due to the benzylic protons H-2 and H-6 and those due to the methylene protons H-4 and H-8 suggest that the stereochemistry at both benzylic centres is identical and since the H-4 and H-8 protons all come below δ5.00, the aryl groups must be equatorial in line with Pelter's criteria (Pelter and Ward 1978). The aromatic protons resonated at δ6.90-δ6.70 as multiplets.

The symmetrical structure of compound (7) is also reflected in the ^{13}C n.m.r. decoupled spectrum where most of the nuclei of the carbon resonances coincided as in table 3. The presence of two hydroxyl groups at C-1 and C-5 caused a downfield shift of about 33.27ppm from 54.24 in a typical furofuran (1) to 87.51ppm in compound (7). C-2 and C-6 were also slightly affected by a shift downfield from 85.61ppm to 86.86ppm in compound (7) and C-4 and C-8 from 71.55ppm to 76.43ppm.

Table 1. *Mass spectra of arboreol and compound (7)*

		Arboreol (3)Relative abundance %		Compound (7) Relative abundance %	
m/e	387	-		-	
	386	0.30	M$^+$	30.0	M$^+$
	370	0.40		0.2	
	369	-		-	
	368	0.40		-	
	338	30.00		0.4	
	310	2.00		-	
	220	1.00		8.0	
	191	-		10.0	
	177	-		16.0	
	164	10.00		7.0	
	161	40.00		-	
	151	-		100.0	
	150	10.00		8.0	
	149	100.00		40.0	
	135	8.00		12.0	
	131	43.00		-	
	121	7.00		16.0	

Table 2. *Proton magnetic resonance spectrum of compound (7) **

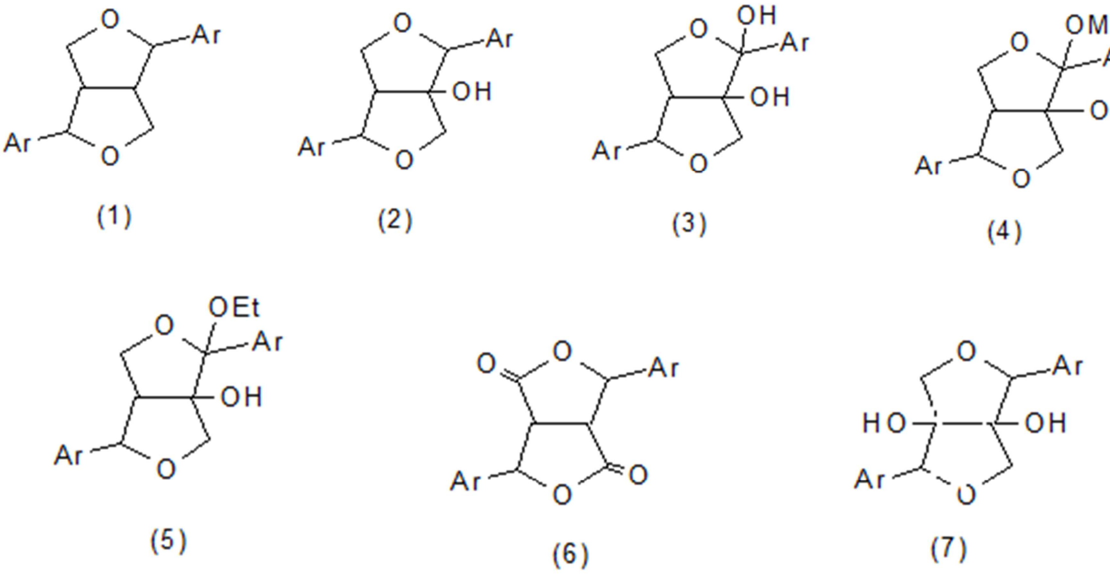
Protons	**δ values (ppm)**
H-1	-
H-5	-
H-2} H-6	4.96 s
H-4} H-8	4.06 s
OCH_2O	5.93 s
Arom.	6.90-6.70 m
OH**	2.45 b.s

*Spectrum run in $CDCl_3$
**Signal disappeared on D_2O shake
s = singlet;m = multiplets;b.s broad singlet

Table 3. *^{13}C n.m.r. spectrum of compound (7) **

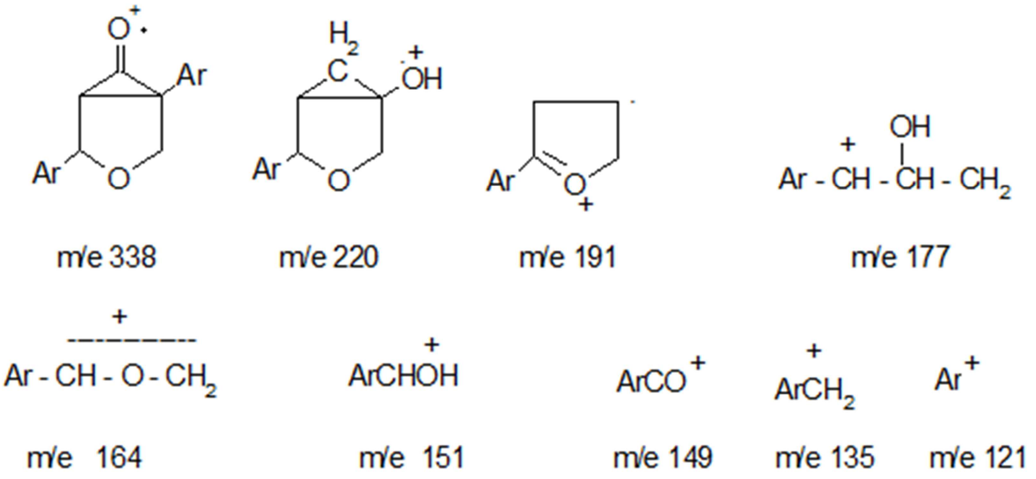
Carbons	**Chemical shifts in (ppm)**
C-1 } C-5	87.51
C-4} C-8	76.43
C-2 } C-6	86.86
C-1^{I}} C-1^{II}	129.52
C-3^{I} 3^{II}} C-4^{I} 4^{II}	147.91
C-2^{I} 2^{II}	107.47
C-5^{I} 5^{II}	108.30
C-6^{I} 6^{II}	120.22
OCH_2O	101.12

*Spectrum run in $CDCl_3$



1-5 &7 Ar=3,4-methylene dioxyphenyl
6 Ar=3-methoxy-4-hydroxyphenyl

Fig. 1. *Structure of sesamin (1) and other hydroxyfurofurans*



Ar = 3,4-methylene dioxyphenyl

Fig. 2. *Fragment ions of compound (7) and arboreol (3)*

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