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PACHARIN: A NEW DIBENZO(2,3-6,7)OXEPIN DERIVATIVE FROM BAUHINIA RACEMOSA LAMK.

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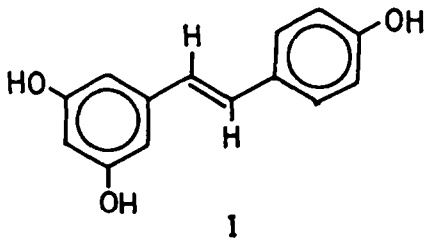
The isolation of resveratrol and a new dibenzoxepin derivative, pacharin, from the heartwood of Bauhinia racemosa Lamk is reported. The structure of pacharin has been established as 1,7-dihydroxy-3-methoxy-2-methyl-dibenzo(2,3-6,7) oxepin (Va) by a study of its chemical and spectroscopic properties, including X-ray analysis.

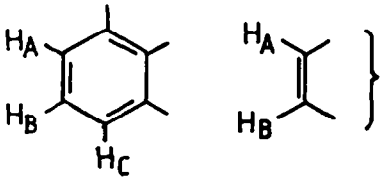
Bauhinia racemosa Lamk. (ver. Telugu, Pachare) is a small deciduous tree[1] belonging to the sub-family Caesalpinaceae in Leguminosae and found in tropical parts of the world. The decoction of its leaves has been used in the treatment of headache and malaria, and its bark as an astringent for diarrhoea and dysentry in Indian medicine[2]. The isolation of β-amyrin and β-sitosterol was reported from its stem bark[3]. The examination of five other Bauhinia species, B.purpurea[4], B.reticulata[5], B.variagata[6], B.vahli[7], and B.malbarika[7] has yielded only free flavonoids or their glycosides. The chemical examination of the heartwood of B.racemosa collected locally is reported herein.

Extraction of the powdered heartwood afforded two crystalline compounds designated as BRE-1 and BRE-2. BRE-1 crystallised from dry acetone as pale yellow needles, m.p. 248°, $C_{14}H_{12}O_3$ and was identified on the basis of its physical and spectral data as trans-resveratrol (I), previously isolated from Arachis hypogaea[8]. Its identity was further supported by a detailed analysis of the ^1H n.m.r. spectra of BRE-1 and its derivatives (Table 1).

BRE-2 crystallised from benzene-acetone as colourless needles, m.p. 210°, $C_{16}H_{14}O_4$ (M^+ 270.0885). It gave a blue colouration with ferric chloride and showed a band at 3480 cm^{-1} in its i.r. spectrum indicating the presence of a hydroxyl group, but showed no band corresponding to a carbonyl group. Its u.v. absorption maxima at 220 nm (logϵ 4.11) and 310 nm (logϵ 4.25) underwent bathochromic shifts of 75 nm and 30 nm respectively on addition of NaOMe but gave no shifts with NaOAc or $AlCl_3$, suggesting involvement of the phenolate ion in extended conjugation. It accounted for one methoxyl in Zeisel's estimation and gave a diacetate, m.p. 170°, $C_{20}H_{18}O_6$ (M^+ 354.1103) and a dimethyl ether, m.p. 109°, $C_{18}H_{18}O_4$ (M^+ 298.1205) indicating the presence of two phenolic hydroxyls. The fourth oxygen could be in the form of a cyclic ether.



I



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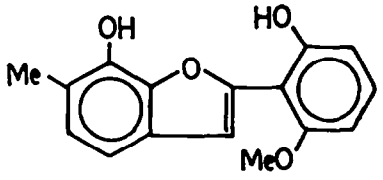
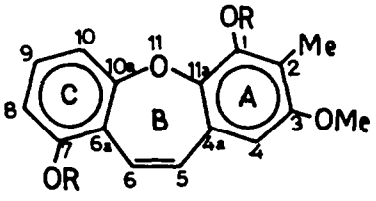
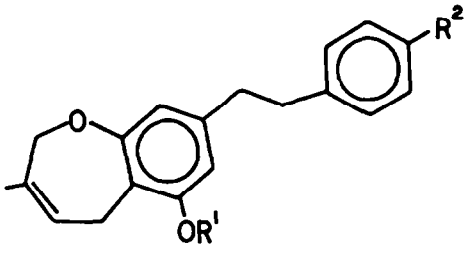


IV



V

a. R = H
b. R = Ac
c. R = Me



VI

a. $R' = H$, $R^2 = H$
b. $R' = Me$, $R^2 = H$
c. $R' = H$, $R^2 = OH$

The ^1H n.m.r. spectrum of pacharin (Table 2) showed the presence of an aromatic methyl group at δ2.02 in addition to an aromatic methoxyl group at δ3.71 and two exchangeable phenolic protons at δ9.45. The aromatic region between 6.29 and 7.12 ppm accounted for 6 protons, one of which appeared as a singlet at δ6.29, while the rest formed a complex multiplet between 6.6 and 7.2 p.p.m. In the spectrum of the diacetate, the aromatic one proton singlet came at δ6.48 suggesting the absence of an adjacent hydroxyl group. In the spectrum of the dimethyl ether the one proton singlet came at δ6.39 while the other five aromatic protons appeared as a complex multiplet between 6.64 and 7.23 p.p.m. Examination of the 360 MHz spectra of the diacetate and the dimethyl ether allowed this five proton multiplet to be analysed in terms of two separate systems of adjacent coupled protons, an ABC system (II) and an AB system (III).

The two doublets centred at 6.73 and 7.03 (J=11.5Hz) are assigned to the two ortho coupled protons of III. Two of the protons in II appear as double doublets (J=8 and 1 Hz) at 6.64 and 6.94 while the third is seen as a triplet (J=8 Hz) at

TABLE 1

^{1}H N.M.R. spectral data of resveratrol and its derivatives

Resveratrol[a]	Acetate[b]	Methylether[b]	Assignment
6.15, 1H,t,J=2Hz	6.86, 1H,t,J=2Hz	6.40, 1H,t,J=2Hz	4-H
6.42, 2H,d,J=2Hz	7.04, 2H,d,J=2Hz	6.68, 2H,d,J=2Hz	2,6-H
6.79, 2H,d,J=8Hz	7.12, 2H,d,J=8Hz	6.93, 2H,d,J=8Hz	3',5'-H
6.91, 2H,d,J=17Hz	7.15, 2H,d,J=13Hz	7.00, 2H,d,J=17Hz	α,α'-H
7.43, 2H,d,J=8Hz	7.52, 2H,d,J=8Hz	7.48, 2H,d,J=8Hz	2',6'-H
9.34, 3H,br., -OH	2.31, 9H,s, OAc	3.85, 9H,s, OMe	

[a]Run in DMSO-d_6
[b]Run in $CDCl_3$

TABLE 2

^{1}H N.M.R. spectral data of Pacharin and its derivatives

Pacharin[a]	Acetate[b]	Methylether[b]	Assignment
7.00, 1H,dd,J=8,2Hz	6.91, 1H,dd,J=8,1Hz	6.94, 1H,dd,J=8,1Hz	10-H
7.12, 1H,t,J=8Hz	7.25, 1H,t,J=8Hz	7.23, 1H,t,J=8Hz	9-H
6.64, 1H,dd,J=8,2Hz	6.86, 1H,dd,J=8,1Hz	6.64, 1H,dd,J=8,1Hz	8-H
6.65, 1H,d,J=11Hz	6.66, 1H,d,J=11.5Hz	6.73, 1H,d,J=11.5Hz	6-H
6.89, 1H,d,J=11Hz	6.72, 1H,d,J=11,5Hz	7.03, 1H,d,J=11.5Hz	5-H
6.29, 1H,s	6.48, 1H,s	6.39, 1H,s	4-H
3.71, 3H,s	3.77, 3H,s	3.99, 3H,s	-OMe
		3.82, 3H,s	
		3.77, 3H,s	
	2.47, 3H,s		-OAc
	2.31, 3H,s		
2.02, 3H,s	2.04, 3H,s	2.16, 3H,s	-CH_3

[a]Run in DMSO-d_6
[b]Run in $CDCl_3$

7.23. The two sets of protons would be expected to belong to two separate aromatic rings or unsaturated systems. A stilbene structure containing a cyclic ether bridge was therefore considered. Thus, for example, the benzofuran structure (IV) would satisfy many of the required structural features but was rejected on the grounds that it was not wholly consistent with the ^{1}H n.m.r. spectrum.

An X-ray analysis was therefore undertaken which revealed the dibenzo(2,3-6,7) oxepin structure (Va). The ^{1}H n.m.r. spectra of pacharin and its derivatives (Vb and Vc) are completely consistent with this structure. Thus, the protons at C-8, C-9 and C-10 in ring C constitute the three proton ABC system while the protons at C-5 and C-6 account for the ortho coupled AB system. The proton at C-4 corresponds to the uncoupled aromatic proton occuring as a singlet.

A study of the ^{13}C n.m.r. spectra of pacharin and its derivatives further corroborated the proposed structure (Table 3). The assignments of the ^{13}C chemical shifts for the respective carbons have been made on the basis of available data for

Table 3

^{13}C N.M.R. spectral data of Pacharin and its derivatives

Pacharin[a]	Methyl ether[b]	Acetate[b]	Assignment
112.26	114.16	119.08	C-10
124.32	124.55	123.45	C-9
100.55	104.99	107.40	C-8
155.19	157.15	148.23	C-7
128.72	129.21	129.45	C-6
129.50	129.86	130.96	C-5
111.56	106.83	118.99	C-4
154.18	154.74	154.61	C-3
113.43	119.99	121.54	C-2
146.88	150.72	141.68	C-1
118.07	121.48	123.86	C-6a
127.90	129.34	128.34	C-4a
138.36	144.24	142.70	C-11a
158.86	159.48	158.67	C-10a
55.49	61.47	55.86	-OMe
	55.84		
	55.76		
8.55	9.10	9.50	-Me
		20.80	-OAc
		21.00	
		170.80	
		171.00	

[a]Run in DMSO-d_6 [b]Run in $CDCl_3$

simple oxepin derivatives[9,10] and the known effects of substituents on the chemical shifts of aromatic systems[11].

Pacharin is thus a novel natural product belonging to the dibenzo(2,3-6,7) oxepin series and having the structure 1,7-dihydroxy-3-methoxy-2-methyl-dibenzo(2,3-6,7) oxepin (Va). No simple oxepin derivatives are known to occur in nature. Three new bibenzyl derivatives having a dihydro-oxepin structure (VI) have recently been isolated from Radula Japonica and R. Tokiensis[12]. Several 4,5-dihydro-dibenzo(2,3-6,7) oxepins and related derivatives have, however, been synthesised and reported to exhibit anti-inflammatory activity, although the details have been patented[13].

The dibenzoxepin derivative may be conceived to have been derived biogenetically from the corresponding stilbene derivative by ring closure. It is therefore significant to note the occurrence of resveratrol in the same plant.

EXPERIMENTAL

^1H and ^{13}C n.m.r. spectra were obtained on Varian HA100 and XL100 instruments respectively. 360 MHz spectra were obtained on the Edinburgh University high field instrument. Mass spectra were obtained using an A.E.I. MS9 spectrometer.

The heartwood of Bauhinia racemosa Lamk. collected from Ananthagiri hills, was dried and powdered. The powdered heartwood (2.5 Kg) was successfully extracted

with hexane, ether and methanol in a soxhlet apparatus.

The ether extract (5 l) was concentrated to 500 ml and left over night. No solid separated out. It was further concentrated to a gummy residue (2.5 g) which was chromatographed on a column of silica gel (100-200 mesh) eluting with hexane, hexane-benzene mixtures and benzene, collecting 250 ml fractions. The hexane and hexane-benzene (9:1) fractions (1-25) did not furnish any crystalline compound. The hexane-benzene (1:1) fractions (25-40) gave BRE-1 as pale red crystals m.p. 248° while the benzene fractions (40-60) furnished BRE-2, m.p. 210°, methanol extract furnished two crystalline compounds in very small quantities which could not be studied. Identification of BRE-1: Resveratrol:

BRE-1 crystallised from dry acetone as pale red crystals, m.p. 248° (resveratrol[9], m.p. 249°). It gave light brown colour with ferric chloride and did not respond to Shinoda's test. Found: C, 73.59; H, 5.40. $C_{14}H_{12}O_3$ requires: C, 73.67; H, 5.35%. UV(EtoH max)nm (log): 221(4.11), 310 (4.25) and 325 (4.24). IR(KBr max) cm^{-1}: 3250, 1605, 1380, 990, 970 and 810. Mass: m/z 228(M^+, 100%), 227(18.5), 226(3.5) 213(4.4), 211(5.5), 210(4.2), 199(5.5), 185(4.8), and 181(13.1).

BRE-1 Acetate:

BRE-1 (50 mg) on acetylation (pyridine, 3 ml+ Ac_2O, 2 ml) gave resveratrol diacetate, crystallised from chloroform-methanol, m.p. 130°. It did not give any colour with $FeCl_3$. Found: C, 67.88; H, 5.2. $C_{20}H_{18}O_6$ requires: C, 67.79; H, 5.12%. IR(KBr max) cm^{-1}: 1760 ($OCOCH_3$), 1610, 1580, 970 and 710. Mass: m/z 354(M^+, 19%), 313(11), 312(57), 271(9), 270(49), 229(15), 228(100), 227(12), 199(4) and 181(12).

BRE-1 methyl ether:

BRE-1 (50 mg) dissolved in dry alcohol was treated with ethereal solutionof diazomethane and kept overnight at 0° to give the methylether as semi solid which resisted cyrstallisation. It did not give any colour with $FeCl_3$. Found: C, 75.46; H, 6.79; OMe, 34.41. $C_{14}H_9(OMe)_3$ requires: C, 75.53; H, 6.71; OMe, 34.44%. IR(KBr max) cm^{-1}: 2835, 1605, 1585, 1510, 990, 970 and 810. Mass: m/z 270(M^+, 100%), 269(9), 239(5), 224(5), 196(6), 195(4), 165(4), 153(5), 152(6), 135(11) and 115(5).

Identification of BRE-2: Pacharin:

BRE-2 crystallised from benzene-acetone as colourless needles, m.p. 210°, R_f 0.15 (Benzene). It gave blue colour with $FeCl_3$ and deep red colour with H_2SO_4. Found: C, 71.10; H, 5.25. $C_{16}H_{14}O_4$ requires: C, 72.10; H, 5.22%. UV(MeoH max) nm (log): 310(4.42), 220(4.10). UV(MeOH + NaOMe max) nm (log): 340(4.38), 295(4.12). No shifts are observed on adding either NaOAc or $AlCl_3$. IR^{nujol} cm^{-1}: 3480, 3420, 2840, 1610, 1010, 860, 840 and 810. Mass: m/z 270(M^+, 100%), 269(4.9), 255(8.5), 241(7.1), 228(4.8), 227(28.1), 212(4.0), 211(8.6), 210(4.8), 199(6.1), 198(4.0), 197(3.0), 184(6.07), 181(5.5), 171(4.1), 169(2.7), 153(4.4), 152(4.7), 141(2.7), 135(8.8), 128(4.7), 127(3.6) and 115(8.3). Accurate mass measurements: 270.0885(M^+, $C_{16}H_{14}O_4$), 227.0701 ($C_{14}H_{11}O_3$), 211.0755($C_{14}H_{11}O_2$). 135.0442($C_8H_7O_2$) and 115.0551(C_9H_7).

BRE-2 acetate: Pacharin diacetate:

BRE-2 (50 mg) on acetylation (pyridine, 3 ml + Ac_2O, 3 ml gave pacharin diacetate crystallised from chloroform-methanol mixture, m.p. 170°, R_f 0.7 (Benzene). Found: C, 67.88; H, 5.23. $C_{20}H_{18}O_6$ requires: C, 67.79; H, 5.12%. IR(KBr max) cm^{-1}: 1760, 1600, 1570, 1490, 1020, 920, 900 and 780. Mass: m/z 354(M^+, 50%), 313(7), 312(36), 271(22), 270(100), 269(5), 241(7), 227(13), 211(5) and 115(6). Accurate mass measurements: 354.1103 (M^+, $C_{20}H_{18}O_6$), 270.0892 ($C_{16}H_{14}O_4$), 227.0708 ($C_{14}H_{11}O_3$), 211.0759 ($C_{14}H_{11}O_2$) and 115.0550 (C_9H_7).

BRE-2 Methylether: Pacharin dimethylether:

To a solution of BRE-2 (50 mg) in DMF (5 ml) methyliodide (1 ml) and freshly

precipitated silver oxide (1 g) were added in small portions during a period of 1 hr. and shaken at room temperature for 24 hr. and the reaction was completed. The reaction mixture was poured into 15 ml of water and extracted with chloroform. The chloroform layer was washed with dilute KCN to remove traces of silver iodide, dried over anhydrous $MgSO_4$ and evaporated to dryness which gave single product crystallised from benzene as pale red prisms, m.p. 109°. Found: C, 72.41; H, 5.94; OMe, 31.25. $C_{15}H_9O(OMe)_3$ requires: C, 72.47; H, 6.08; OMe, 31.20. IR_{max} cm^{-1}: 2835, 1610, 1460, 1229, 1280, 1120, 810 and 740. Mass: m/z 298(M^+, 100%), 255(15), 240(8), 239(5), 224(5), 223(6) and 149(12). Accurate mass measurements: 298.1205 (M^+, $C_{18}H_{18}O_4$), 255.1016 ($C_{16}H_{15}O_3$) and 149.0600 ($C_9H_9O_2$). Crystal data: (From single crystal photographs and diffractometry) CuKα, λ = 1.54056Å); $C_{16}H_{14}O_4$, F.W.=270.29, monoclinic, P 2/n, a=17.170 (1), b=4.9154(7), c=15.514(1) Å, β=98.085(3), V=1296.3Å^3, Z=4, Dc=1.38g cm^{-3}, μ = 0.78 mm^{-1}. Intensity data, structure determination and refinement: The specimen used was a fragment of

Table 4: Fractional Positional Coordinates and Biso for atoms. E.S.d.'s are given in parentheses.

Atom	X	Y	Z	Biso
C(1)	0.86320(12)	-0.2105(4)	0.52823(13)	2.85(9)
C(2)	0.78382(12)	-0.2791(4)	0.51270(13)	2.85(10)
C(3)	0.73370(12)	-0.1390(5)	0.56087(13)	2.93(11)
C(4)	0.76034(12)	0.0592(5)	0.62039(13)	3.07(11)
C(4a)	0.84031(12)	0.1302(4)	0.63449(13)	2.80(10)
C(5)	0.86794(13)	0.3501(5)	0.69534(13)	3.17(10)
C(6)	0.93983(13)	0.3726(5)	0.74068(14)	3.26(10)
C(6a)	1.00494(12)	0.1827(4)	0.74193(13)	2.89(9)
C(7)	1.06038(12)	0.1552(5)	0.81714(13)	3.22(11)
C(8)	1.12240(14)	-0.0253(6)	0.82020(15)	4.12(13)
C(9)	1.13086(14)	-0.1819(6)	0.74858(18)	4.41(13)
C(10)	1.07800(14)	-0.1593(5)	0.67290(16)	3.92(12)
C(10a)	1.01732(12)	0.0222(5)	0.67095(13)	2.91(10)
O(11)	0.96949(8)	0.0627(3)	0.59066(8)	3.18(8)
C(11a)	0.89067(11)	-0.0086(4)	0.58726(12)	2.69(10)
O(12)	0.91330(9)	-0.3480(3)	0.48250(10)	3.62(8)
C(13)	0.75575(13)	-0.4899(5)	0.44572(14)	3.77(11)
O(14)	0.65501(8)	-0.2150(4)	0.54307(10)	3.83(9)
C(15)	0.60076(14)	-0.0811(7)	0.59107(18)	5.38(18)
O(16)	1.04936(10)	0.3131(4)	0.88711(10)	4.18(9)
H(4)	0.722(1)	0.153(4)	0.650(1)	2.4(4)
H(5)	0.824(1)	0.485(5)	0.707(1)	3.4(5)
H(6)	0.949(1)	0.533(5)	0.787(1)	4.2(5)
H(8)	1.162(1)	-0.040(5)	0.877(2)	5.2(6)
H(9)	1.178(1)	-0.328(6)	0.751(2)	5.9(7)
H(10)	1.082(1)	-0.273(5)	0.623(2)	4.6(6)
H(12)	0.964(2)	-0.233(7)	0.489(2)	9.5(10)
H(131)	0.789(2)	-0.657(6)	0.453(2)	7.0(7)
H(132)	0.709(2)	-0.537(7)	0.450(2)	8.6(9)
H(133)	0.761(2)	-0.412(8)	0.386(2)	11.3(11)
H(151)	0.551(2)	-0.202(5)	0.577(2)	6.6(7)
H(152)	0.620(2)	-0.099(6)	0.658(2)	7.4(8)
H(153)	0.601(2)	0.144(7)	0.578(2)	9.0(9)
H(16)	1.091(2)	0.285(6)	0.931(2)	8.5(9)

extreme dimensions 0.13 and 0.33 mm. The unit cell constants were obtained by least-squares analysis of the diffractometer settings of 37 well centred reflections with $102^{o}<2\theta<128^{o}$. The relative intensities of the independent reflections with $2\theta<130^{o}$ were measured with a Picker four-circle diffractometer using Ni-filtered CuKα radiation. The $\theta-2\theta$ Scan method was used, and individual reflection profiles were analysed as described by Grant and Gabe (1978)[14]. The standard deviations of the measured intensities were evaluated from counting stastics, and only those for which $I > 3\sigma(I)$ were used in the analysis. These numbered 1650, of a possible 2213. No absorption corrections were applied.

Table 5: Bond lengths (Å) and bond angles involving Non hydrogen atoms. E.S.d.'s in bond lengths is .003Å and that in bond angles ≈ .2°.

C(1) - C(2)	1.392	C(1) - C(2) - C(13)	120.0
C(1) - O(12)	1.365	C(3) - C(2) - C(13)	123.3
C(1) - C(11a)	1.387	C(2) - C(3) - C(4)	122.4
C(2) - C(3)	1.398	C(2) - C(3) - O(14)	114.5
C(2) - C(13)	1.498	C(4) - C(3) - O(14)	123.0
C(3) - C(4)	1.376	C(3) - C(4) - C(4a)	120.4
C(3) - O(14)	1.392	C(4) - C(4a)- C(5)	120.2
C(4) - C(4a)	1.404	C(4) - C(4a)- C(11a)	117.6
C(4a)- C(11a)	1.389	C(5) - C(4a)- C(11a)	122.1
C(4a)- C(5)	1.469	C(4a)- C(5) - C(6)	126.2
C(5) - C(6)	1.337	C(5) - C(6) - C(6a)	127.2
C(6) - C(6a)	1.454	C(6) - C(6a)- C(10a)	123.7
C(6a)- C(10a)	1.395	C(6) - C(6a)- C(7)	120.2
C(6a)- C(7)	1.405	C(6a)- C(7) - C(8)	121.3
C(7) - C(18)	1.382	C(6a)- C(7) - O(16)	116.8
C(7) - O(16)	1.369	C(8) - C(7) - O(16)	121.9
C(8) - C(9)	1.376	C(7) - C(8) - C(9)	120.0
C(9) - C(10)	1.384	C(8) - C(9) - C(10)	120.6
C(10)- C(10a)	1.369	C(9) - C(10)- C(10a)	118.5
O(14)- C(15)	1.432	C(10)- C(10a)-O(11)	117.4
C(10a)-O(11)	1.406	C(10)- C(10a)-C(6a)	123.4
O(11)- C(11a)	1.392	C(6a)- C(10a)-O(11)	119.0
		C(10a)-O(11)- C(11a)	116.2
C(2)-C(1)-C(11)	121.4	C(1) - C(11a)-C(4a)	121.4
C(2)-C(1)-O(12)	117.6	C(1) - C(11a)-O(11)	116.3
C(11a)-C(1)-O(12)	121.0	C(4a)- C(11a)-O(11)	122.0
C(1)-C(2)-C(3)	116.7	C(3) - O(14) -C(15)	117.2

Table 6: Selected torsion angles (°) with e.s.d.'s in parentheses.

C(4a) - C(5) - C(6) - C(6a)	- 2.1(4)
C(5) - C(6) - C(6a)- C(10a)	31.3(4)
C(6) - C(6a)- C(10a)-O(11)	6.6(3)
C(6a) - C(10a)-O(11)- C(11a)	-67.8(2)
C(10a)- O(11)- C(11a)-C(4a)	66.6(3)
O(11) - C(11a)-C(4a)- C(5)	- 3.9(3)
C(11a)- C(4a)- C(5) - C(6)	-29.9(4)
O(11) - C(11a)-C(1) - O(12)	6.2(3)

The structure was readily solved by direct methods (MULTAN; Germain, Main and Woolfson, 1971)[15]. Refinement was by block-diagonal least-squares, minimising $\Sigma W \Delta F^2$, where $1/W = \sigma^2(Fo) + 0.0005(Fo)^2$. The hydrogen atoms were determined from a difference-fourier synthesis, and included in the refinement. The parameters refined were atomic coordinates and temperature factors (anisotropic for C and O). Scale factor, and extinction coefficient (Larson, 1970).[16] The final R index (for observed reflections only) was 0.038 (including unobserved, 0.056; Rw = 0.0575).

The computer program system has been described by Larson and Gabe (1978).[17] The atomic scattering factors were taken from International Tables, Vol IV (1974).[18]

Discussion: The molecular skeleton is shown in Fig. 1. The oxepin ring has an approximate C_2 symmetry, with the C_2 axis passing through the atom O(11) and bisecting the C(6)-C(5) bond.

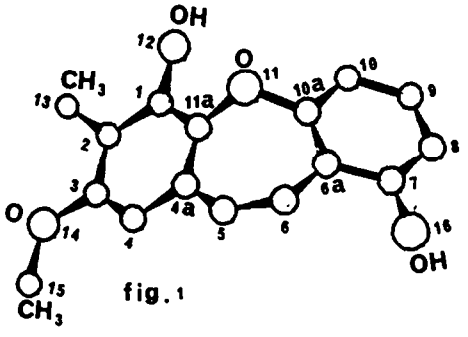


fig.1

REFERENCES

1 J.S. Gamble, `Flora of the presidency of Madras` published by Botanical survey of India, Calcutta, Vol.I, P. 277 (1967).

2 R.N. Chopra, I.C. Chopra and S.L. Nayar, `Glossary of Indian Medicinal Plants', C.S.I.R., New Delhi, p. 34 (1956).

3 Anand Prakash and Rathanlal Khosa, Curr.Sci., 45, 705 (1976).

4 Reena Ramachandran and Bherwam C. Joshi, Curr.Sci., 36, 574 (1967).

5 D.C.J. Rasate, J.Pharm.Chim., 28, 435 (1938).

6 Nabiel, A.M. Saleh and Moheb S.I. Shak, Phytochemistry., 15, 835 (1976).

7 S. Duret and R.R.Paris, Plant.Med.Phytother., 11, 213 (1971).

8 J.L. Nigam, Phytochemistry., 15, 1791 (1976).

9 Rainer Wehner and Harald Gunther, Chem.Ber., 107(9), 3149-51 (1974) (Ger).

10 St. Berger and A. Rieker, Org. Magn.Resonance., 6, 78-84 (1974).

11 Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, George C. Lavy and Gordon L. Nelson, John Wiley and Sons. Inc. P. 81 (1972).

12 Y. Asakawa, Reiji Takeda, Masao Toyota and T. Takemoto, Phytochemistry., 20(4), 858-59 (1981).

13 Yemabe Shigera and Fujimoto Yasuo, Nippon Chemiphar.Co. Ltd.; Braz Pedido PI 79, 01272 (Cl.CO7D 491/04). C.A., 95, 97770Y (1981).

14 Grant, D.F. and Gabe, E.J., J. Appl. Cryst., 11, 114 (1978).

15 Germain, G., Main, P. and Woolfson, M.M., Acta cryst., A27, 368 (1971).

16 Larson, A.C. `Crystallographic computing', Munksgaard. Copenhagen, pp. 291-294 (1970).

17 Larson, A.C. and Gabe, E.J., `Computing in crystallography' Delft University Press, Delft, Holland, pp 81-89 (1978).

18 `International Tables for X-ray crystallography', Vol. IV, Kynoch Press, Birmingham (1974).