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ISOLATION OF CANDIRONE: A NOVEL PENTAOXYGENATION PATTERN IN A NATURALLY OCCURRING 2-PHENYL-4H-1-BENZOPYRAN-4-ONE FROM TEPHROSIA CANDIDA

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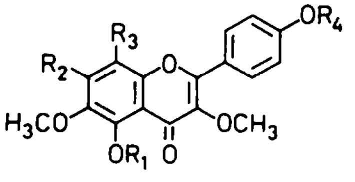
Abstract - Two flavones having very similar physical behaviour and spectral data have been isolated as minor constituents from the seeds of Tephrosia candida. Based upon a detailed and critical study of their mass spectra, extent of shifts in their UV spectra, X-ray diffraction studies, and preparation of their derivatives, the structures of these compounds have been established; one was found to be penduletin (1) and the other 5-hydroxy-2-(4-hydroxyphenyl)-3,6,8-trimethoxy-4H-1-benzopyran-4-one (2), for which the name candirone is proposed. To the best of our knowledge the latter is a new compound and this type of oxygenation pattern is not known earlier among natural flavones.

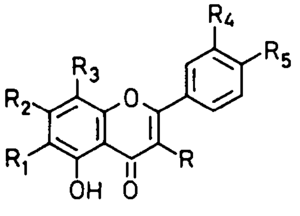
INTRODUCTION

Several naturally occurring 2-phenyl-4H-1-benzopyran-4-ones are known to be agents that reduce the induction of cancer in animals by functioning as MFO-systems.[1,2] Kupchan et al.[3] have isolated two anti-cancer agents (5, ED_{50} 2.4 µg/ml and 6, ED_{50} 2.5 µg/ml) from the alcoholic extracts of Baccharis sarothroides. Bittner et al.[4] have isolated a new compound, 5-hydroxy-2-(3,4-dihydroxyphenyl)-3,6,7,8-tetramethoxy-4H-1-benzopyran-4-one (7), having significant activity against human carcinoma of the nasopharynx (4.4 x 10^{-1}) from the aerial parts of Gutierrezia resinosa. From the ethanol extract of the aerial parts of Tephrosia candida, Sarin et al.[5] have isolated a flavonol glycoside (8) having activity against human epidermoid carcinoma of the nasopharynx in tissue culture (9 KB). All these flavonols (5 to 8) have a similarity in their structure - the C-3 methoxyl group and the C-5 hydroxyl group. In view of these observations we have undertaken the investigation of the seeds of Tephrosia candida. The isolation of caffeic acid, candidin, pongachin, 6a,12a-dehydrodeugelin, tephrosin, 12a-hydroxyrotenone, β-sitosterol and its glucoside has earlier been reported by us[6] from this source. Along with the isolation of these two compounds having very similar behaviour were isolated: penduletin (1) and 5-hydroxy-2-(4-hydroxyphenyl)-3,6,8-trimethoxy-4H-1-benzopyran-4-one (2), for which we propose the name candirone. Both the compounds are 5-hydroxy-3-methoxyflavones and the structure elucidation of these is the subject of this report. Candirone (2) is a flavone with a novel pentaoxygenated structural pattern, while this is the first report of the isolation of penduletin (1) from this species.

RESULTS AND DISCUSSION

Both penduletin (1) and candirone (2) analysed for $C_{18}H_{16}O_7$ [M^+ 344 (100%) for both] and they behaved similarly on TLC upon development in several solvent systems, but the m.p.'s of the two compounds (222° for 1 and 232-34° for 2) were





(1) $R_1 = R_4 = H, R_2 = OCH_3, R_3 = H$

(2) $R_1 = R_4 = H, R_2 = H, R_3 = OCH_3$

(3) $R_1 = R_4 = COCH_3, R_2 = OCH_3, R_3 = H$

(4) $R_1 = R_4 = COCH_3, R_2 = H, R_3 = OCH_3$

(5) $R = R_5 = OCH_3, R_1 = R_3 = H, R_2 = R_4 = OH$

(6) $R = R_1 = R_5 = OCH_3, R_2 = R_4 = OH, R_3 = H$

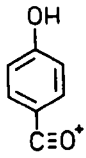
(7) $R = R_1 = R_2 = R_3 = OCH_3, R_4 = R_5 = OH$

(8) $R = R_2 =$ O-rhamnosyl, $R_1 = OH, R_3 = R_4 = H, R_5 = OCH_3$

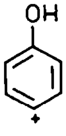
(9) $R = R_4 = H, R_1 = R_2 = R_3 = OCH_3, R_5 = OH$

found to be different.

From their characteristic colour reactions with Mg/HCl both 1 and 2 were indicated to be flavone derivatives and their UV spectra exhibited very similar λ MeOH/max values (268 and 339 nm for 1, 269 and 337 nm for 2), which was also typical of the flavonoid skeleton. Both 1 and 2 on acetylation with excess of acetic anhydride/pyridine formed diacetates, thereby showing the presence of two -OH groups in each of them. The presence of a chelated hydroxyl group at C-5 in both the compounds was indicated in the UV spectrum by the observed bathochromic shift in the presence of $AlCl_3$/HCl shift reagent. With the shift reagent NaOAc their UV spectra did not exhibit any bathochromic shift, thus indicating the absence of any free hydroxyl group at the C-7 position in them. However, the UV spectra of 1 and 2 exhibited a large bathochromic shift upon addition of sodium methoxide shift reagent, indicating the presence of a 4'-hydroxy group in both compounds, which was substantiated by the appearance of two doublets (J=9 Hz) at δ 6.95 and 7.99, each for 2H in case of 1 and at δ 7.00 and 8.02 in case of 2, characteristic of the A_2B_2 pattern in the NMR spectrum of the two compounds (1) in DMSO-d_6 and 2 in CD_3COCD_3). The presence of a 4-hydroxyphenyl B-ring in both 1 and 2 was confirmed by the peaks at m/z 121 and 93 in their MS, corresponding to the ions a and b, respectively, formed by the RDA cleavage of the molecules.



a



b

The ^{1}H-NMR spectrum of 1 and 2 showed three singlets between δ 3.75 and 3.97 for three methoxyl groups and a singlet at δ 6.83 (in 1) and at δ 6.80 (in 2) for 1H. Mears and Mabry[7] have reported that a bathochromic shift of the order of 17-20 nm in the UV spectrum on addition of $AlCl_3$ shift reagent indicates the presence of 6-oxygenation in 5-hydroxyflavones, while the absence of an oxygenated function at C-6 results in a bathochromic shift of 40-60 nm in similar compounds. As 1 and 2 showed the bathochromic shifts with $AlCl_3$ of 20 nm and 11 nm, respectively, it was inferred that a methoxyl group is present at the C-6 position in both of them. The presence of $-OCH_3$ group at the C-6 position in 1 and 2 was substantiated as the MS of both showed an $(M-15)^+$ peak at m/z 329 [(30%) for 1 and

(46%) for 2]; the $(M-CH_3)^+$ peak is characteristic of 6-methoxyflavones.[8] There are three possibilities in which the remaining two methoxyls could be located, *viz*. at C-7 and C-8; at C-3 and C-8; and at C-3 and C-7. The first possibility, *i.e*. the methoxyl groups at C-7 and C-8 positions, was ruled out because the m.p. and spectral data of 5,4'-dihydroxy-6,7,8-trimethoxyflavone[9] (9) do not tally with the m.p. and spectral data of either 1 or 2. This substitution pattern was also ruled out as the MS of both 1 and 2 showed the A-ring RDA cleavage fragments at m/z 181 [1 or m (15.3%) for 1 and n (8%) for 2] and at m/z 153 [o (20%) for 1 and p (8%) for 2], thereby showing that the A ring in both the compounds is only trioxygenated.

From this discussion it follows that the second methoxyl group is present at the C-3 position in both the compounds. The presence of an $-OCH_3$ group at the C-3 position was supported by the presence of an $M-COCH_3)^+$ peak in the MS of both 1 and 2 at m/z 301 [(13%) for 1 and (8%) for 2]; the $(M-43)^+$ peak is characteristic of 3-methoxyflavones.[8] The MS of 1 and 2 also contained an intense $(M-H)^+$ peak at m/z 343 [(15%) for 1 and (28.5%) for 2], which is also characteristic of 3-methoxyflavones.[8] By fixing the position of the remaining methoxyl group penduletin and candirone could thus be either 1 or 2.

To confirm which compound is which, we resorted to X-ray diffraction studies. The crystals of 1 used in the X-ray investigation were obtained upon spontaneous evaporation of a solution of the compound in glacial acetic acid. The crystals contained one molecule of water for each molecule of penduletin. Despite many attempts compound 2 could not be obtained in a form suitable for X-ray investigation. The X-ray diffraction studies (Fig. 1) confirmed the structure of penduletin as 1.

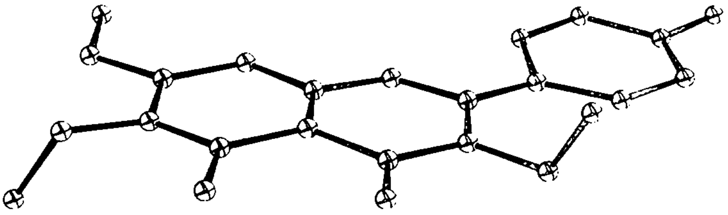


Fig. 1. Computer-generated perspective drawing (ORTEP) of the penduletin molecule determined by X-ray diffraction.

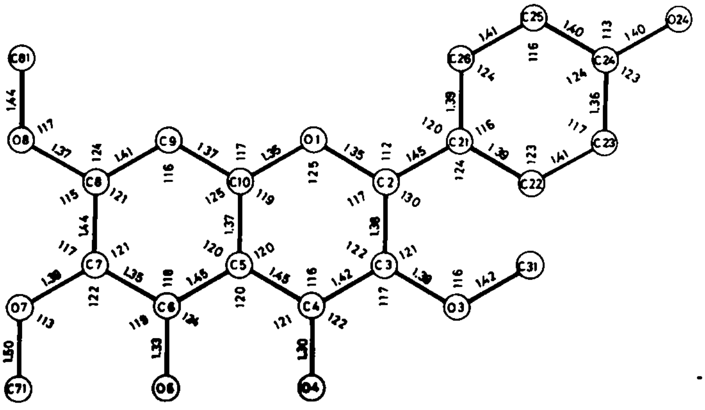


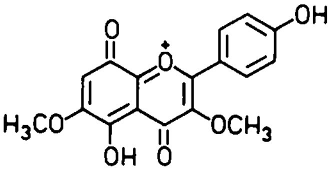
Fig. 2. Bond distances (Å), angles (°) and the atomnumbering scheme for 1. Estimated standard deviations for the bond distances and angles are 0.03-0.04 Å and 2-3°, respectively. The crystal water (027, not shown) makes hydrogen bonds to 024 (2.72(3) Å) and to 04 (2.74(3) Å, 2.91(4) Å).

All the spectral data of 1 and its m.p. were found to be similar to those reported for penduletin.[10,11] This is the first report of any X-ray work on penduletin and its occurrence in *T. candida*.

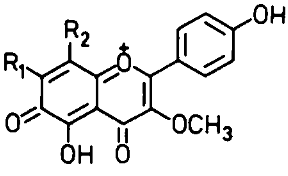
The condensed ring system (A), (O1 C10) in penduletin is planar (Fig. 1, Fig. 2). The dihedral angle made by the benzene ring and (A) is 3.0°. The methoxy group O8-C81 is in the ring plane (A). The methyl groups C31 and C71 are on opposite sides of (A), indicated by the dihedral angles C2-C3-O3-C31: 92(3)° and C8-C7-O7-C71: 75(4)°. Fractional atomic coordinates are listed in Table 1.

As the compound 2 differs from 1 in m.p., extent of bathochromic shift with $AlCl_3$ shift reagent in its UV spectrum (20 nm for 1 and 11 nm for 2), position of -OH signal in the IR spectrum (3350 cm^{-1} in 1 and 3100 cm^{-1} in 2) and the intensities of a few fragments in its mass spectrum, structure 2 could be proposed for candirone. With Gibb's reagent[12] 1 furnished a deep blue colour, while 2 generated a dull brown colour; this supported the structure 1 and 2 for penduletin and candirone, respectively.

The presence of an $-OCH_3$ group at C-8 in 2 was further supported by the fact that the intensity (46%) of the $(M-15)^+$ peak was higher in the MS of 2 as compared to that in 1 (30%). This is because in 2 two $(M-CH_3)^+$ fragments (c and d) are possible, while in 1 only one such fragment (e) is possible. Furthermore, the intensity (28.5%) of the $(M-1)^+$ peak in the MS of 2 was almost twice of that in 1 (15%); it is due to the fact that there are two equally stable fragments (f and g) corresponding to the $(M-H)^+$ peak at m/z 343 in 2, whereas only one such fragment (h) is possible in 1. This further supports the location of an $-OCH_3$ group at the C-8 position in compound 2. A small peak at m/z 315 (5%), due to the $(M-CH_3, -CH_2)^+$ ion wàs observed in the mass spectrum of 2, but not in that of 1. This peak also supported the location of an $-OCH_3$ group at the C-8 position in 2 as there will be two stable $(M-29)^+$ fragments (i and j) in case of 2 as against only one such fragment (k) in the case of 1.

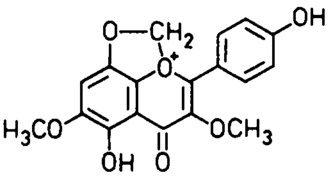


c

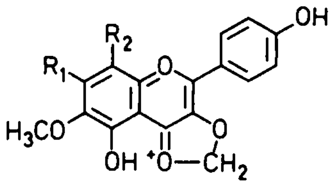


d R_1 = H, R_2 = OCH_3

e R_1 = OCH_3, R_2 = H



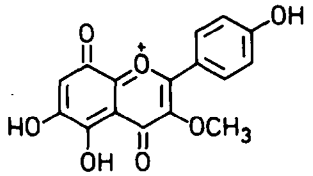
f



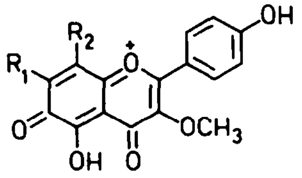
g R_1 = H, R_2 = OCH_3

h R_1 = OCH_3, R_2 = H

The difference in the extent of bathochromic shift with $AlCl_3$ shift reagent in the UV spectrum of 1 and 2 could be attributed to conjugation as a result of which



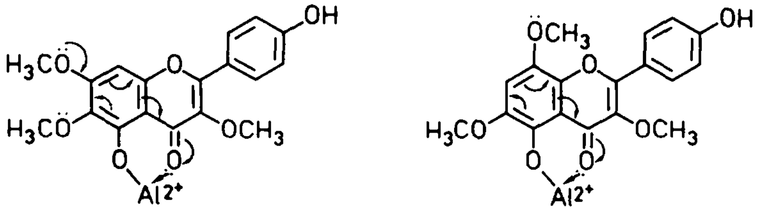
i



j R_1 = H, R_2 = OH

k R_1 = OH, R_2 = H

auxochromic effect could be exerted. The C-7 methoxyl group is in conjugation with the chromophoric carbonyl group as depicted in Fig. 2 (a), hence it acts as an auxochrome and shifts the UV maxima to higher wavelength in presence of $AlCl_3$ in 1 (20 nm); the C-8 methoxyl group is not in conjugation [Fig. 3 (b)]; thus, the $AlCl_3$-induced bathochromic shift observed in compound 2 (11 nm) is less.



(a) (b)

Fig. 3. Extent of conjugation in 1 and 2 upon reaction with $AlCl_3$.

Finally, the structure of 2 was confirmed by preparing its diacetate (4), whose m.p. 162°C differed from that of 1 (3, m.p. 156-57°C; lit.[10] m.p. of penduletin diacetate 157-58°C). The structure of the acetate of 2 was supported by its ^1H-NMR and mass spectra. The ^1H-NMR spectrum of 4 exhibited five singlets each for 3H at δ 2.34 $(-O-\underset{\overset{\|}{O}}{C}-CH_3)$, 2.51 $(-O-\underset{\overset{\|}{O}}{C}-CH_3)$, 3.80 $(-OCH_3)$, 3.86 $(-OCH_3)$, and 3.98 $(-OCH_3)$, a singlet at δ 6.86 due to H-7 and two doublets (J=9 Hz), each for 2H at δ 7.24 and 8.10, attributed to H-3' & H-5' and H-2' & H-6', respectively; its mass spectrum showed the prominent peaks at m/z 428 (M^+, 19), 386 (100), 385 (17), 371 (15.5), 343 (17), and 301 (5).

Thus, candirone was confirmed as 5-hydroxy-2-(4-hydroxyphenyl)-3,6,8-trimethoxy-4H-1-benzopyran-4-one (2). This is a new compound as it has neither been synthesized earlier nor isolated from any natural source. To the best of our knowledge this is the first example of 3,5,6,8,4'-pentaoxygenation pattern in a naturally occurring flavone and could be of interest from the point of view of its biogenesis. The name candirone has been suggested by us for this new compound.

Table 1. Fractional atomic coordinates and thermal parameters for 1 with estimated standard deviations in parentheses.

atom	x	y	z	B_{eq}
O1	0.3514(7)	0.1095(6)	0.4232(0)	5.0(1.5)
O3	0.3875(8)	0.2471(6)	0.8452(72)	5.0(1.4)
O4	0.2439(8)	0.2606(6)	0.6451(78)	5.4(1.5)
O6	0.1243(8)	0.2158(6)	0.3791(81)	6.1(1.7)
O7	0.0620(9)	0.1242(7)	0.0457(80)	6.4(1.9)
O8	0.1387(8)	0.0276(7)	-0.0898(81)	5.6(1.6)
O24	0.6796(9)	0.0754(7)	0.8154(80)	6.7(1.9)
O27	0.2708(9)	0.3457(7)	0.1156(81)	6.6(1.7)
C2	0.3895(11)	0.1516(8)	0.5841(97)	4.0(1.8)
C3	0.3525(11)	0.2024(10)	0.6696(87)	4.3(1.7)
C4	0.2780(12)	0.2116(8)	0.5823(89)	4.6(1.9)
C5	0.2431(11)	0.1646(9)	0.3944(97)	4.4(1.8)
C6	0.1655(10)	0.1688(10)	0.3117(105)	5.4(2.4)
C7	0.1344(11)	0.1229(9)	0.1529(91)	4.3(1.7)
C8	0.1765(12)	0.0707(9)	0.0767(106)	5.6(2.6)
C9	0.2515(11)	0.0660(9)	0.1637(96)	4.6(1.8)
C10	0.2805(11)	0.1137(10)	0.3281(106)	5.3(2.2)
C21	0.4634(119	0.1332(9)	0.6649(100)	4.6(2.0)
C22	0.5134(13)	0.1682(10)	0.8346(95)	5.8(2.3)
C23	0.5866(12)	0.1513(11)	0.8943(100)	5.4(2.2)
C24	0.6085(13)	0.0979(10)	0.7735(95)	5.6(2.3)
C25	0.5627(12)	0.0603(11)	0.5889(108)	5.4(2.4)
C26	0.4906(13)	0.0805(9)	0.5392(111)	5.6(2.7)
C31	0.4203(13)	0.2914(9)	0.6471(105)	5.0(2.2)
C71	0.0119(14)	0.0862(13)	0.2524(129)	7.9(3.6)
C81	0.1793(14)	-0.0248(10)	-0.1783(122)	6.6(2.9)

EXPERIMENTAL

M.p.'s were determined on a Nalge micro melting point apparatus and are uncorrected, UV spectra were recorded on Perkin-Elmer model-554 spectrophotometer, IR spectra on a Shimadzu model-435 spectrophotometer, ^{1}H-NMR spectra were recorded on Perkin Elmer R-32 (90 MHz) or on Jeol JNM FX-200 FT NMR spectrometer with TMS as the internal standard and mass spectra were recorded on a Varian Mat 331 A instrument.

Isolation of penduletin (1) and candirone (2). The dried and powdered seeds (2 kg) of Tephrosia candida were extracted with hot petroleum ether (60-80°C), benzene and ethanol, successively. The concentrate of the petrol and benzene extracts (15 g) was chromatographed over silica gel (500 g); elution of the column with benzene-ethyl acetate (7:3) yielded 2. The concentrate of the alcohol extract was macerated several times with dry ether to remove a dark tarry material; the concentrate of the ether soluble portion (30 g) on column chromatography over silica gel (1 kg) and elution with petrol-ethyl acetate (7:3) gave 1.

Penduletin (1) crystallized from methanol and from glacial acetic acid as yellow crystalline solid (15 mg); m.p. 222° (lit.[10] m.p. 216-217°); brownish-green colour with alc. $FeCl_3$ and pink colour with Mg/HCl; λ MeOH/max: 268, 339; $+AlCl_3$: 272, 359; $+AlCl_3/HCl$: 272, 356; +NaOAc: 270, 340; +NaOMe: 271, 394 nm; ν KBr/max: 3350, 1640, 1580, 1540, 1460, 1420, 1340, 1260, 1200, 1170, 1060, 990, 800, 760 cm^{-1}; δ H (DMSO-d_6, 200 MHz): 3.75 (s, 3H, $-OCH_3$), 3.83 (s, 3H, $-OCH_3$), 3.95 (s, 3H, $-OCH_3$), 6.83 (s, 1H, H-8), 6.95 (d, J=9 Hz, 2H, H-3' & H-5'), 7.99 (d, J=9 Hz, 2H, H-2' & H-6'), 12.60 (s, 1H, C-5 OH); EIMS m/z (%): 345 $(M+1)^+$ (6), 344 (M^+) (100), 343 $(M-1)^+$ (15), 329 (30), 326 (5.1), 325 (18.1), 301 (13.5), 181 (15.3), 153 (20.0), 121 (45.1), 93 (17.2).

X-ray diffraction. The crystals of 1 used in the X-ray investigation were obtained upon spontaneous evaporation of a glacial acetic soln of the compound. The crystals contain water in the ratio $1/H_2O = 1/1$. The obtained crystals were very faintly diffracting and only a minority of the measured reflections could be considered as observed. A crystal with the dimensions 0.4 x 0.07 x 0.07 mm was selected. Space group $Pna2_1$ (No. 33) from systematic extinctions. The reflections were measured with an Enraf-Nonius CAD-4F diffractometer, using graphite-monochromatized MoKα radiation (λ = 0.71073 Å). Lattice parameters were determined from setting angles for 25 reflections with $7.29 < \theta < 13.89$, (a = 18.208(2), b = 22.686(7), and c = 4.013(2) Å). The reflections (h $0 \rightarrow 25$, k $0 \rightarrow 31$, l $0 \rightarrow 5$) in the range $2° < \theta < 30°$ were measured with a mixed ω/θ scan technique. A reflection was designated not observed if $I \leq 2.5\sigma(I)$. With this criterion only 603 out of 2731 (independently measured) reflections were regarded as observed. Lorentz and polarization corrections were applied, but no extinction or absorption corrections were made.

The structure was solved by direct methods using the SHELX-76 system.[13] Refinement and analysis of the structure were performed with the X-RAY-76 system,[14] computer: SPERRY 1100/72. The quantity minimized was $\Sigma w||F_o|-|F_c||^2$ by using unit weight. Contributions from unobserved reflections were included if $F_c > F_o$. The positional H-parameters were calculated but not refined. The position of the methyl H-atoms were calculated under the assumption that one H-atom in each methyl group is part of an H-C-O-C= trans configuration. Atomic scattering factors for the neutral atoms were taken from International Tables for X-ray Crystallography.[15] The final R index ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ was rather high ($R = 0.14$) due to the low quality of the data set. Maximum and minimum in final difference density map: 0.41 and -0.53 e/Å^3, respectively.

The final R index was very high ($R = 0.14$) due to the poor quality of the crystal. However, with all bond distances and angles, as well as temperature factors, refining to acceptable values, together with a final difference density map showing maximum and minimum values 0.41 and -0.53 e/Å^3, respectively, away from atomic sites, the structure determinations appear to be correct.

Candirone (2) crystallized from methanol as yellow silky needles (25 mg); m.p. 232-234°; R_f (28°) 0.20 (benzene-acetone, 19:1) and 0.40 (benzene-ethyl acetate, 7:3); brownish-green colour with alc. $FeCl_3$; pink colour with Mg/HCl; λ MeOH/max: 269, 337; +$AlCl_3$: 260, 348; +$AlCl_3$/HCl: 270, 352; +NaOAc: 268, 339; +NaOMe: 270, 392 nm; ν KBr/max: 3100, 1640, 1580, 1540, 1460, 1420, 1340, 1260, 1200, 1170, 1060, 990, 800, 760 cm^{-1}; δ H (CD_3COCD_3, 200 MHz): 3.78 (s, 3H, $-OCH_3$), 3.86 (s, 3H, $-OCH_3$), 3.97 (s, 3H, $-OCH_3$), 6.80 (s, 1H, H-7), 7.00 (d, J=9 Hz, 2H, H-3' & H-5'), 8.02 (d, J=) Hz, 2H, H-2' & H-6'), 9.26 (s, 1H, C-4' OH), 12.64 (s, 1H, C-5 OH); EIMS m/z (%): 345 $(M+1)^+$ (20), 344 $(M)^+$ (100), 343 $(M-1)^+$ (28.5), 329 (46), 326 (6), 325 (20), 315 (5), 301 (8), 181 (8), 153 (8), 125 (3), 121 (13.1), 93 (4).

Diacetate of candirone (4). Candirone (8 mg) was dissolved in pyridine (0.2 ml) and acetic anhydride (0.6 ml) was added to it. The mixture was just warmed and kept for 24 hr at 30°C. On usual work up, 4 crystallized from acetone - n-hexane as a white solid (5 mg), m.p. 162°C; δ H ($CDCl_3$, 200 MHz): 2.34 (s, 3H, $-OCOCH_3$), 2.51 (s, 3H, $-OCOCH_3$), 3.80 (s, 3H, $-OCH_3$), 3.86 (s, 3H, $-OCH_3$), 3.98 (s, 3H, $-OCH_3$), 6.86 (s, 1H, H-7), 7.24 (d, J=9 Hz, 2H, H-3' & H-5'), 8.10 (d, J=9 Hz, 2H, H-2' & H-6'); EIMS m/z (%): 428 $(M)^+$ (19), 387 (23), 386 (100), 385 (17), 371 (15.5), 343 (17), 329 (19.5), 325 (11), 315 (5), 301 (5), 285 (3.8), 181 (5), 167 (6), 153 (3.8), 121 (5.9).

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