Methylation of demethylmacrosporin (**1**). Pulverized K_2CO_3 (500 mg) and MeI (2 ml) were added to a soln of **1** (33 mg) in Me_2CO (4 ml). After refluxing for 10 min, the reaction mixture was poured into ice-water, acidified with dil. HCl to pH 3, extracted with EtOAc, and dried (Na_2SO_4). The evapd residue was recrystallized from Me_2CO to give a 7-*O*-methylmacrosporin (**6**) (23 mg).

7-O-Methylmacrosporin (**6**). Yellow needles (Me_2CO); mp 261–264°, IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1670, 1630 (CO), 1600, 1320; EIMS (probe) 70 eV, *m/z* (rel. int): 298.0849 $[M]^+$ ($C_{17}H_{14}O_5$ requires 298.0842, 100); ^1H NMR ($CDCl_3$): δ2.35 (3H, *br s*, 6-Me), 3.93 (3H, *s*, OMe), 4.02 (3H, *s*, OMe), 6.66 (1H, *d*, $J = 2.5$ Hz, 2-H), 7.35 (1H, *d*, $J = 2.5$ Hz, 4-H), 7.63 (1H, *s*, 8-H), 8.03 (1H, *q*, $J = 1.0$ Hz), 12.84 (1H, *s*, 1-OH).

Methylation of macrosporin (**2**). Compound **1** (37 mg) was reacted with K_2CO_3 and MeI in Me_2CO and worked-up in the same manner described above to give compound **5** (25 mg). Compound **5** was identical with the compound derived from **1** by comparison of the ^1H NMR and IR spectra and the TLC behaviour and by mmp.

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REFERENCES

1. Kawahara, N., Nakajima, S., Yamazaki, M. and Kawai, K. (1989) *Chem. Pharm. Bull.* **37**, 2592.
2. Mehrlich, F. P. and Fitzpatrick, H. M. (1935) *Mycologia* **27**, 543.
3. Rao, P. N. (1966) *Mycopathol. Mycol. Appl.* **28**, 137.
4. De Hoog, G. S. and Oorschot, C. A. N. van (1983) *Proc. K. Ned. Akad. Wet.* **C86**, 55.
5. Routien, J. B. (1957) *Mycologia* **49**, 188.
6. Becker, A. M., Rickards, R. W., Schmalzl, K. J. and Yick, H. C. (1978) *J. Antibiot.* **31**, 324.
7. Stoessl, A. (1967) *Chem. Commun.* 307.
8. Stoessl, A. (1969) *Can. J. Chem.* **47**, 767.
9. Wheeler, M. M., Wheeler, D. M. S. and Peterson, G. W. (1975) *Phytochemistry* **14**, 288.
10. Suemitsu, R., Kitagawa, N., Horie, S., Kazawa, K. and Harada, T. (1978) *Agric. Biol. Chem.* **42**, 1801.
11. Stoessl, A. and Unwin, C. H. (1979) *Tetrahedron Letters* 2481.
12. Sivanesan, A. (1987) Micological Papers, No. 158, CAB International Mycological Institute, Wallingfood, p. 261.
13. Suemitsu, R., Nakajima, M. and Miura, M. (1961) *Agric. Biol. Chem.* **25**, 100.
14. Kettner, M., Nemec, P., Kovac, S. and Balanova, J. (1973) *J. Antibiot.* **26**, 692.

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REVISION OF THE STRUCTURE AND ABSOLUTE CONFIGURATION OF CASSIALACTONE*

SUSUMU KITANAKA, KOREHARU OGATA† and MICHIO TAKIDO

College of Pharmacy, Nihon University, Narashinodai, Funabashi-shi, Chiba 274, Japan; †The Chemical Analysis Center, Chiba University, Yayoi-cho, Chiba-shi, Chiba 260, Japan

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Key Word Index—*Cassia obtusifolia*; Leguminosae; naphthalenic lactone; cassialactone; structure revision; X-ray analysis; conformational isomer; excition chirality method.

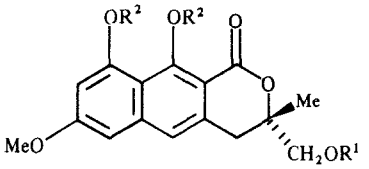
Abstract—The structure of cassialactone isolated from the seeds of *Cassia obtusifolia* was revised as (*S*)-3,4-dihydro-9,10-dihydroxy-3-hydroxymethyl-7-methoxy-3-methyl-1*H*-naphtho[2,3-*c*]pyran-1-one based on X-ray analysis and its CD spectrum.

INTRODUCTION

In a previous paper [1], we reported the isolation of cassialactone (**1**), mp 196–197.5°, $C_{16}H_{16}O_6$, $[\alpha]_D^{22}$ −17.2°, having the structure 8-methoxy-4-methyl-4,10,11-trihydroxy-naphth[2,3-*c*]oxepin-1(3*H*)-one from seeds of *Cassia obtusifolia* L. The compound was isolated together with torosachrysone (**2**) [1, 2] which had the structure 3,4-dihydro-3,8,9-trihydroxy-6-methoxy-1(2*H*)-anthracenone. Thus, from the viewpoint of biogenesis, as the structure of **1** has been reported to have a naphth[2,3-*c*]oxepin skeleton, **2** may be obtained by Baeyer–Villiger-type oxidation.

*Part 26 in the series 'Studies on the Constituents of Purgative Crude Drugs'. For Part 25 see Kitanaka, S., Takahashi, M. and Takido, M. (1990) *Phytochemistry* **29**, 350.

Recently, the cassialactone molecule has been considered to have a 3,4-dihydronaphth[2,3-*c*]pyrane-1-one skeleton as well, but these structures cannot be distinguished from NMR spectra alone. Therefore, using X-ray Biovit analysis, an attempt was made to determine the precise structure of the acetate of **1**.



1 $R^1 = R^2 = H$
1a $R^1 = R^2 = Ac$
1b $R^1 = H$, $R^2 = Me$
1c R^1 = *p*-methoxybenzoyl, $R^2 = Me$

RESULTS AND DISCUSSION

By acetylation with dry acetic acid and pyridine at room temperature, **1** gave triacetate (**1a**), as prisms, mp 255–257°, $C_{22}H_{22}O_9$ ([M]$^+$ 430.1280), these crystals were suitable for X-ray analysis. The structure of **1a** finally determined is given in Fig. 1, where the small circles represent hydrogen atoms. The final atomic parameters are listed in Table 1. The M_r of **1a** is 430.1 but molecules with two different structures (conformers A and B, Fig. 1) are included as one unit cell, so that the M_r of **1a** obtained was 860.2 per unit cell. Conformers A and B have a common configuration at C-3 and 3′ but the molecular conformations of the two functional groups (methyl and acetoxymethyl) combining at C-3 and 3′ differ. That is, in the case of conformer A, a methyl and an acetoxymethyl group are located axially to equatorially, respectively, whereas those of conformer B are located equatorially to axially, respectively. The relationship between conformers A and B involves different conformations at C-3, constituting conformational isomers [3]. The absolute configuration of **1** at C-3 was determined by the excition chirality method [4–7], and it was found that on methylation with diazomethane, **1** gave the dimethyl ether (**1b**), which was converted to a monobenzoate (**1c**) with *p*-methoxybenzoyl chloride and pyridine. The CD curve of **1c** exhibits strongly positive first ($\Delta\varepsilon$ +41.4, 268 nm) and negative second ($\Delta\varepsilon$ −22.5, 247 nm) Cotton effects. These are due to the coupling between the ^1B_b transition of the naphthalene chromophore and the ^1L_a transition of the benzoyl chromophore, showing that the long axes of the naphthalene ring and the *p*-methoxybenzoyl group are twisted in a clockwise manner. This CD behaviour indicated the *S* configuration at C-3 in **1c** and therefore the *S* configuration in **1**. Based on these findings, the structure of **1** was revised to be (*S*)-3,4-dihydro-9,10-dihydroxy-3-hydroxymethyl-7-methoxy-3-methyl-1*H*-naphtho[2,3-*c*]pyran-1-one.

EXPERIMENTAL

Cassialactone triacetate (**1a**). Cassialactone (**1**) (3 mg) was acetylated with Ac_2O–pyridine at room temp. to give a triacetate (**1a**), which was then recrystallized from *n*-hexane–EtOAc to give prisms, mp 255–257°. High-resolution MS: *m/z* 430.1280 [M]$^+$; calc. for $C_{22}H_{22}O_9$: 430.1262; UV λ_{max}^{MeOH} nm (log ε): 244 sh (4.30),

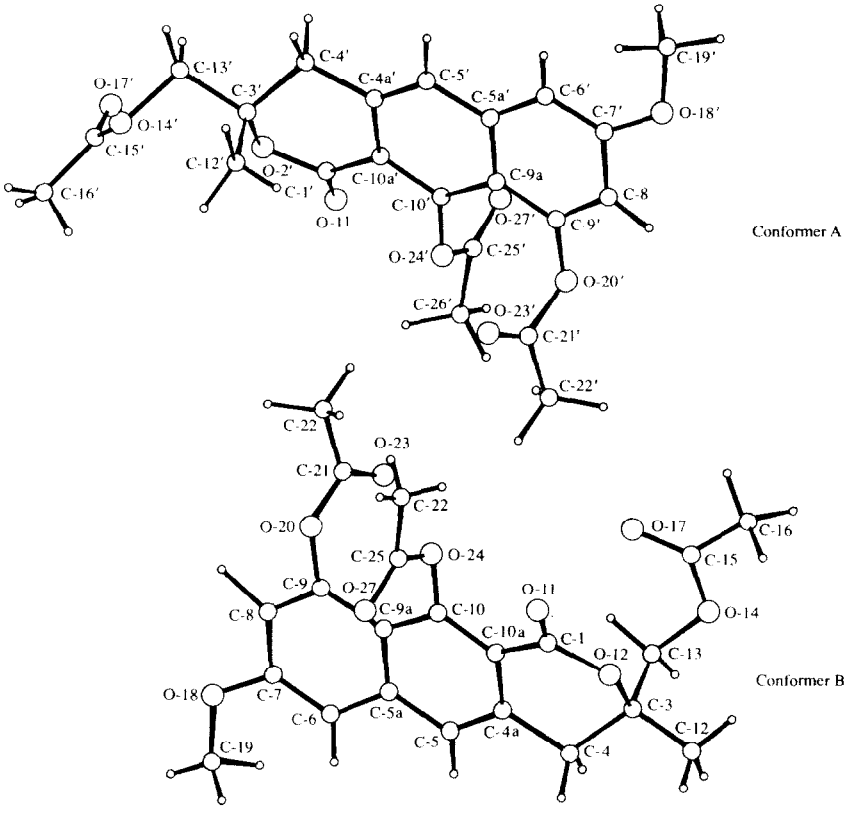


Fig. 1. Solid-state conformation of cassialactone triacetate (**1a**).

Table 1. Positional and thermal parameters for the non-hydrogen atoms of compound **1a**

Atom	Conformer A				Atom	Conformer B			
	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*
C-1	0.4716 (8)	0.2755 (8)	0.7728 (8)	3.0	C-1′	−0.4709 (8)	0.7232 (7)	0.2344 (9)	2.9
O-2	0.5995 (5)	0.2062 (5)	0.7341 (6)	2.9	O-2′	−0.5878 (6)	0.7850 (5)	0.2909 (7)	3.5
C-3	0.6902 (9)	0.2662 (8)	0.6796 (10)	3.6	C-3′	−0.6762 (8)	0.7201 (7)	0.3292 (9)	2.8
C-4	0.6843 (8)	0.3790 (8)	0.7817 (9)	3.1	C-4′	−0.6811 (8)	0.6211 (7)	0.2172 (8)	2.6
C-4a	0.5412 (8)	0.4611 (7)	0.7977 (8)	2.6	C-4a′	−0.5417 (7)	0.5318 (7)	0.1936 (8)	2.5
C-5	0.5137 (8)	0.5913 (7)	0.8363 (8)	2.8	C-5′	−0.5140 (8)	0.4076 (7)	0.1579 (8)	2.7
C-5a	0.3822 (8)	0.6702 (7)	0.8503 (8)	2.5	C-5a′	−0.3789 (7)	0.3247 (7)	0.1401 (8)	2.6
C-6	0.3542 (7)	0.7999 (7)	0.8969 (8)	2.6	C-6′	−0.3559 (9)	0.2001 (8)	0.0964	3.3
C-7	0.2237 (8)	0.8800 (8)	0.9100 (9)	3.2	C-7′	−0.2275 (9)	0.1215 (8)	0.0808 (10)	3.6
C-8	0.1189 (8)	0.8344 (8)	0.8744 (9)	3.0	C-8′	−0.1167 (9)	0.1628 (9)	0.1257 (10)	3.9
C-9	0.1392 (8)	0.7156 (8)	0.8267 (9)	3.0	C-9′	−0.1401 (8)	0.2851 (7)	0.1671 (9)	2.8
C-9a	0.2751 (7)	0.6230 (7)	0.8216 (8)	2.2	C-9a′	−0.2678 (9)	0.3719 (8)	0.1754 (10)	3.1
C-10	0.3096 (8)	0.4954 (8)	0.7879 (8)	2.9	C-10′	−0.3032 (7)	0.5075 (7)	0.2010 (7)	2.1
C-10a	0.4373 (7)	0.4152 (7)	0.7812 (8)	2.5	C-10a′	−0.436498	0.5853 (7)	0.2896 (8)	2.8
O-11	0.4018 (6)	0.2185 (5)	0.7800 (7)	3.6	O-11′	−0.4035 (7)	0.7805 (6)	0.1981 (8)	4.8
C-12	0.8241 (9)	0.1650 (9)	0.6891 (13)	4.7	C-12′	−0.6253 (11)	0.6632 (11)	0.4740 (10)	4.9
C-13	0.6464 (10)	0.3016 (10)	0.5276 (9)	4.2	C-13′	−0.8187 (10)	0.8226 (9)	0.3339 (12)	4.7
O-14	0.6493 (6)	0.1853 (6)	0.4487 (7)	4.1	O-14′	−0.8091 (6)	0.9036 (5)	0.4653 (6)	3.7
C-15	0.5314 (10)	0.1677 (10)	0.5276 (11)	4.8	C-15′	−0.8082 (9)	1.0183 (8)	0.4427 (11)	4.0
C-16	0.5445 (16)	0.0371 (14)	0.3708 (18)	9.2	C-16′	−0.7884 (12)	1.0840 (9)	0.5795 (11)	5.3
O-17	0.4271 (8)	0.2474 (8)	0.4549 (10)	6.7	O-17′	−0'8239 (8)	1.0622 (6)	0.3258 (8)	5.5
O-18	0.1894 (6)	0.9996 (5)	0.9610 (6)	3.6	O-18′	−0.1892 (7)	−0.0029 (6)	0.0341 (9)	5.3
C-19	0.2938 (10)	1.0444 (8)	1.0181 (10)	4.0	C-19′	−0.2922 (11)	−0.0485 (9)	−0.0273 (14)	5.3
O-20	0.0280 (5)	0.6772 (5)	0.7981 (6)	3.3	O-20′	−0.0278 (5)	0.3203 (5)	0.1993 (6)	3.1
C-21	−0.0098 (8)	0'.6669 (9)	0.6607 (10)	3.9	C-21′	0.0027 (9)	0.3430 (8)	0.3402 (10)	3.4
C-22	−0.1373 (10)	0.6378 (10)	0.6423 (12)	5.2	C-22′	0.1297 (9)	0.3780 (10)	0.3510 (12)	4.7
O-23	0.0565 (8)	0.6746 (8)	0.5663 (7)	6.0	O-23′	−0.0608 (6)	0.3321 (7)	0.4331 (7)	4.5
O-24	0.2054 (5)	0.4411 (5)	0.7659 (6)	2.8	O-24′	−0.2026 (5)	0.5556 (5)	0.2341 (6)	2.8
C-25	0.1546 (8)	0.4087 (8)	0.8833 (9)	3.2	C-25′	−0.1634 (7)	0.6018 (8)	0.1203 (9)	3.0
C-26	0.0602 (9)	0.3465 (8)	0.8409 (10)	3.7	C-26′	−0.0719 (10)	0.6766 (9)	0.1710 (11)	4.5
O-27	0.1899 (6)	0.4332 (7)	0.9979 (6)	4.2	O-27′	−0.1998 (6)	0.5881 (7)	−0.0014 (7)	4.7

255 (4.35), 306 sh (3.68), 317 (3.72), 347 sh (3.54); IR ν_{max}^{KBr} cm^{-1}: 3418, 1771, 1746, 1719, 1629, 1573, 1467, 1428; ^1H NMR ($CDCl_3$) δ: 1.44 (3H, *br s*, Me-3), 2.00, 2.41 and 2.47 (each 3H, *s*, OAc), 3.00 and 3.33 (each 1H, *br s*, 4-H), 3.93 (3H, *s*, OMe), 4.15 and 4.25 (each 1H, *br s*, $-CH_2OH$), 6.85 and 6.99 (1H each, 2*d*, $J = 2.4$ Hz, H-6 and −8), 7.45 (1H, *br s*, H-5); EIMS: *m/z* 430 $[M]^+$ (6%) with the base peak at *m/z* 346.

Crystal data of **1a**. $C_{22}H_{22}O_9$, $M_r = 430.1, 860.2$ (2 molecules), triclinic, space group P1, $a = 10.639(3)$, $b = 11.311(2)$, $c = 9.429(2)$ Å, $\alpha = 93.70(2)$, $\beta = 94.09(3)$, $\gamma = 70.14(2)$, $V = 1063.5$ Å^3, $Z = 1$ (2 mol/unit cell), $D_{calcd} = 1/342$ g cm^{-3}, $(CuK_a) = 15405$ Å. A total of 4460 unique independent intensities were measured within the range $3° < 2\theta < 150°$ on a four-circle diffractometer (Rigaku AFC-5). The structure was solved by the direct method using MULTAN 80 (UNICS III system) and refined by the least-squares method, using the 1657 reflections for which $|Fo| > 3\sigma|Fo|$. The final *R* value was 5.64%.

Cassialactone dimethyl ether (**1b**). A soln of **1** (8.5 mg) in MeOH (2 ml) was methylated with CH_2N_2 at 4° for 15 hr. The solvent was then evapd. The residue was submitted to prep. TLC with C_6H_6–EtOAc (1:1), a major band recrystallized from *n*-hexane–EtOAc to give prisms, mp 195°. High resolution MS: *m/z* 332.1253 $[M]^+$, calc for $C_{18}H_{20}O_6$: 332.1258. UV λ_{max}^{MeOH} nm (log ε): 258 (4.61), 308 sh (3.79), 325 (3.84), 350 (3.90). IR ν_{max}^{KBr} cm^{-1}: 3416, 1686, 1620, 1571. ^1H NMR ($CDCl_3$) δ: 1.26 (3H, *br s*, Me-3), 2.73 and 3.49 (1H, *d*, $J = 16.3$ Hz, H-4), 3.58 and 3.78 (each 1H, *d*, $J = 11.9$ Hz, $-CH_2OH$), 3.83, 3.91, and 3.97 (each 3H, *s*, OMe), 6.50 and 6.61 (each 1H, *d*, $J = 2.4$ Hz, H-6 and H-8).

Cassialactone dimethyl ether benzoate (**1c**). Cassialactone diMe ether (**1b**) (3.5 mg) was treated with *p*-methoxybenzoyl chloride (5 mg) in pyridine (1 ml) at 4° overnight. The reaction mixt was evapd *in vacuo*. The residue was purified by silica gel CC using *n*-hexane–EtOAc (3:2) to give **1c** (4.1 mg) as a amorphous compound. High-resolution MS: *m/z* 466.1638 $[M^+]$ calc. for $C_{26}H_{26}O_8$: 466.1626; UV λ_{max}^{MeOH} nm (log ε): 212 (4.46), 258 (4.73), 313 sh (3.76), 327 (3.78), 352 (3.84); CD (*c* 1.76×10^{-5}, MeOH, Δε): 310 sh (+2.0), 268 (+41.4), 257 (0), 247 (−22.5), 224 (0), 216 (+4.62), 209 (0); IR ν_{max}^{KBr} cm^{-1}: 2928, 2852, 1718, 1618, 1605, 1570, 1509; ^1H NMR ($CDCl_3$) δ: 1.47 (3H, *br s*, Me-3), 3.01 and 3.34 (each 3H, *d*, $J = 16.0$ Hz, H-4), 3.83 and 3.91 (each 3H, *s*, OMe), 3.97 (6H, *s*, OMe × 2), 4.33 and 4.50 (each 1H, *d*, $J = 11.7$ Hz, $-CH_2OBz$), 6.50 and 6.61 (each 1H, *d*, $J = 2.4$ Hz, H-6 and −7), 6.82 and 7.87 (each 1H, *d*, $J = 9.0$ Hz, H-Bz).

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REFERENCES

1. Kitanaka, S. and Takido, M. (1981) *Phytochemistry* **20**, 1951.
2. Takido, M., Takahashi, S., Masuda, K. and Yasukawa, K. (1977) *Lloydia* **40**, 191.
3. Noguchi, H., Sankawa, U. and Iidaka, Y. (1978) *Acta Cryst.* **B34**, 3273.
4. Harada, N. and Nakanishi, K. (1972) *Acc. Chem. Res.* **5**, 257.
5. Harada, N., Chen, S. L. and Nakanishi, K. (1975) *J. Am. Chem. Soc.* **97**, 5345.
6. Harada, N., Tamura, Y. and Uda, H. (1976) *J. Am. Chem. Soc.* **98**, 5408.
7. Harada, N., Tamura, Y. and Uda, H. (1978) *J. Am. Chem. Soc.* **100**, 4029.

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CIRRHOPETALIN, A PHENANTHRENE DERIVATIVE FROM *CIRRHOPETALUM ANDERSONII*

P. L. MAJUMDER* and MAUSUMI BASAK

Department of Chemistry, University College of Science, 92 Acharya Prafulla Chandra Road, Calcutta 700009, India

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Key Word Index—*Cirrhopetalum andersonii*; Orchidaceae; cirrhopetalin; 7-hydroxy-4-methoxy-2,3-methylene dioxy phenanthrene.

Abstract—Cirrhopetalin, a new phenolic compound, isolated from the orchid *Cirrhopetalum andersonii* was shown to be 7-hydroxy-4-methoxy-2,3-methylenedioxy phenanthrene mainly from spectroscopic evidence.

INTRODUCTION

Our continued search for new phytochemicals from Indian orchids has resulted in the isolation of a new phenanthrene derivative, designated as cirrhopetalin, from *Cirrhopetalum andersonii*. It was shown to have the structure **1a**.

RESULTS AND DISCUSSION

Cirrhopetalin, $C_{16}H_{12}O_4$ ([M]$^+$ *m/z* 268), mp 142°, showed UV absorptions, λ_{max}^{EtOH} 206, 258, 284 and 344 nm (log ε 4.40, 4.89, 4.29 and 2.95) typical of phenanthrene derivatives [1–6]. The presence of a phenolic hydroxyl group was indicated by its characteristic colour reactions, alkali induced bathochromic shifts of its UV maxima $\lambda_{max}^{EtOH-0.1\ M\ NaOH}$ 217, 239, 270 and 305 nm (log ε 4.37, 4.48, 4.90 and 4.19), its IR band at ν_{max} 3185 cm^{-1}, and was confirmed by the formation of a monoacetyl derivative, $C_{18}H_{14}O_5$ ([M]$^+$ *m/z* 310), mp 139°, with acetic anhydride and pyridine.

The ^{1}H NMR spectrum of cirrhopetalin showed signals for a phenolic hydroxyl group (δ5.06, 1H, *s*; deuterium exchangeable), an aromatic methoxyl (δ4.11, 3H, *s*), a methylenedioxy function (δ6.08, 2H, *s*) and six aromatic protons. Of the signals for the aromatic protons the pair of one-proton doublets at δ7.46 (J = 8.82 Hz) and 7.53 (J = 8.82 Hz) is reminiscent of H-9 and H-10 of phenanthrene derivatives [1–5, 7, 8], and the one-proton doublet at δ9.41 (J = 9.06 Hz) is typical of H-5 or H-4 of such compounds [1, 4, 5, 7, 8]. Assignment of the latter signal to H-5 implied that while C-4 and C-7 of the compound must contain an oxygen substituent, its C-6 was unsubstituted. The one-proton doublet of the doublet at δ7.14 (J_1 = 9.05 Hz and J_2 = 2.87 Hz) may then be assigned to H-6 which coupled with both H-5 and H-8.

The one-proton doublet at δ7.18 (J = 2.87 Hz) may thus be attributed to H-8. The remaining aromatic proton signal at δ7.01 (1H, *s*) was then assigned to H-1, bearing oxygen substituents at C-2, C-3 and C-4. In the ^{1}H NMR spectrum of cirrhopetalin acetate only the signals at δ7.14 and 7.18 corresponding to H-6 and H-8 of the parent compound showed downfield shifts of 0.16 and 0.36 ppm respectively, while that at δ7.01 remained almost unchanged, and the signals for H-9 and H-10 collapsed to a singlet at δ7.57. Thus H-6 and H-8 of cirrhopetalin must be flanked by the lone hydroxyl group at C-7, and ruled out the placement of the hydroxyl function at either C-2 or C-4. The absence of a hydroxyl group at C-4 was also indicated by the fact that its signal for H-5 showed a slight downfield shift (0.12 ppm) in the spectrum of its acetate, which, instead, would have been shifted upfield by

*Author to whom correspondence should be addressed.