TWO NEW CONSTITUENTS FROM *UVARIA MICROCARPA*

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Abstract Two new polyhydroxy heptene derivatives, named microcarpin A and microcarpin B, were isolated from *Uvaria microcarpa* Champ ex Benth. Their structures were determined by the means of spectroscopy and chemistry.

Air-dried stem bark of *Uvaria microcarpa* Champ ex Benth. (Annonaceae) collected from Xishuangbanna, were extracted with ethanol(95%) at room temp.. The crude extract was fractionated by a series of solvent partitions to give three extract parts. The MeOH / H_2O(90%) fraction was chromatographed on silica gel column to afford two new polyhydroxy heptene derivatives named microcarpin A and microcarpin B.

Microcarpin A (760mg, 0.0095%), $C_{21}H_{22}O_7$, HRMS 386.1366, FAB-MS, m / z387$[M+H]^+$, colourless needles(acetone), mp 71-73℃ ; $[\alpha]_D^{26.8} = -11.6°$ (c 1.32, MeOH); The data of UVλ_{max}^{EtOH}nm(lgε): 203(4.16), 228.5(4.42), 273.5(3.36), 280(3.29) suggested the presence of conjugated system. The IR spectrum showed there were characteristic absorptions of hydroxyl groups (3100-3500cm^{-1}), two carbonyls of ester (1715cm^{-1}, C=O; 1685cm^{-1}, C=O; 1270cm^{-1}, C-O) and phenyl ring (1590, 1450, 705cm^{-1}). Thus the IR and UV spectra suggested the presence of benzoyloxy group. The ten aromatic protons in the ^1H NMR spectrum (see Table1) indicated two benzoyloxy groups. The ^{13}C NMR spectrum (see Table2) showed the presence of three methines and two methenes all bearing oxygen atoms, and a disubstituted double bond. So its structure was proposed as dibenzoyloxy trihydroxy heptene.

The complete acetylation of microcarpin A(^1H NMR, see Table1) confirmed the presence of three hydroxyl groups. Using ^1H-^1H COSY and ^{13}C-^1H COSY, the correlated couplings of 4-H and 5-H, 3-H and 2-H, 5-H and 6-H, 6-H and 7-H, 1-H and 2-H had been confirmed. The 2D-COLOC spectrum, C-1′ correlated with 1-H and C-1″ correlated with 7-H indicated C-1 and C-7 were substituted by benzoyloxy groups. (So C-2, C-5, C-6 were substituted by

hydroxyl groups.) In addition, the correlated coupling of C–1′ and C–3′(C–1″ and C–3″) confirmed the presence of benzoyloxy groups again. On the other hand, in ^{1}H NMR, δ6.55ppm(3–H) and δ6.84ppm (4–H), $J_{3,4}$ = 16.0Hz indicated a *trans* relationship at C–3 and C–4. Based on these facts, microcarpin A was identified as 3E–1, 7–dibenzoyloxy–2, 5, 6–trihydroxyheptene. The mass spectral fragmentation pattern also supported the structure (Fig.1).

Microcarpin B (320mg, 0.004%), $C_{21}H_{22}O_7$, HRMS 386.1366, FAB–MS, m / z387[M+H]$^+$, colourless needles (acetone); mp 111.5–113.5℃ ; $[\alpha]_D^{26.1} = -13.20°$ (c 0.341, MeOH); The UV and IR spectra of microcarpin B provided nearly the same absorption as microcarpin A. The resemblance exposed they were a couple of isomers. The ^{1}H NMR spectrum (see Table1) like that of microcarpin A, displayed signals for ten aromatic protons. The most striking difference was the appearance of δ6.39ppm (dd 5–H), the same proton signals were at δ4.91ppm in microcarpin A. Another two–proton signals shifted upfield from δ5.06ppm to δ4.25ppm. That showed a benzoyl group had transfered from C–7 to C–5. The data of ^{13}C NMR (see Table2) also indicated C–5 shifted downfield 3.2ppm to δ76.8ppm and C–7 shifted upfield 3.8ppm to δ64.0ppm. The 2D–COLOC spectrum, C–1″ correlated with 5–H confirmed the transfer. The double bond of microcarpin B also changed a little. δ6.51ppm(3–H) and δ6.81ppm(4–H), $J_{3,4}$ = 15.6Hz also indicated a *trans* relationship. The analysis confirmed the structure for microcarpin B: 3E–1, 5–dibenzoyloxy–2, 6, 7–trihydroxyheptene. EIMS supported its structure (Fig.2).

The configurations at C–2, C–5, C–6 have not been defined.

The plants of the genus *Uvaria* have provided an array of compounds possessing polyhydroxy cyclohexane skeletons[1–4], but the two constituents microcarpin A and B possessing non–cycle skeletons had not been seen.

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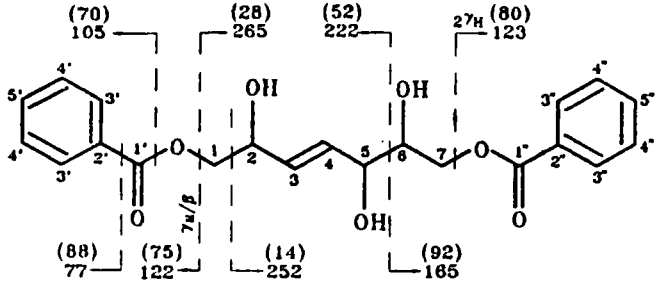


microcarpin A

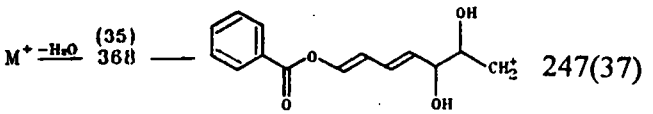
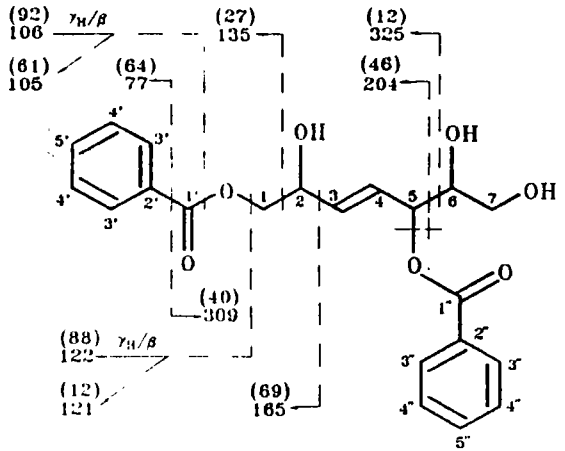


Fig.1. Microcarpin A and the Mass Spectral Cleavage



microcarpin B

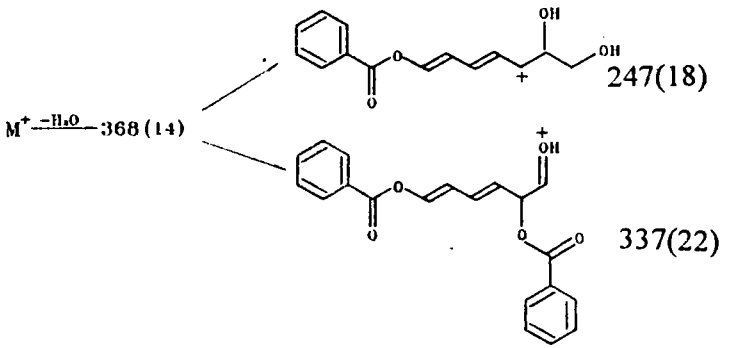


Fig 2. Microcarpin B and the Mass Spetral Cleavage

Table 1. ^{1}H NMR Data of Microcarpin A, B [400MHz, in C_5D_5N, δ(ppm), J(Hz)] and Acetylates (in $CDCl_3$)

H	microcarpin A		microcarpin B		acetylated microcapin A	aceylated microcarpin B
	δ	J	δ	J	δ	δ
H-1, 2H	4.67 m		4.65 m		4.34 m	4.44 m
H-2, 1H	5.00 m		4.95 td	$J_{2,3}$= 5.6	5.35 dt	5.36 m
				$J_{2,4}$= 1.4		
H-3, 1H	6.55 ddd	$J_{3,5}$= 1.4	6.51 ddd	$J_{3,4}$=15.6	5.86 dd	5.57 dd
		$J_{3,4}$=16.0		$J_{3,2}$= 5.2		
		$J_{3,2}$= 5.6		$J_{3,5}$= 0.7		
H-4, 1H	6.84 ddd	$J_{4,3}$=16.0	6.81 ddd	$J_{4,3}$=15.6	5.87 dd	5.93 dd
		$J_{4,5}$= 5.6		$J_{4,5}$= 7.2		
		$J_{4,2}$= 1.4		$J_{4,2}$= 1.4		
H-5, 1H	4.91 brt	$J_{5,4}$= 5.6	6.39 dd	$J_{5,6}$= 5.0	5.59 brt	5.65 brt
		$J_{5,3}$= 1.4		$J_{5,4}$= 7.2		
		$J_{5,6}$= 6.0		$J_{5,3}$= 0.7		
H-6, 1H	4.53 dt	$J_{6,5}$= 6.0	4.61 dd	$J_{6,5}$= 5.0	5.65 m	5.59 m
H-7, 2H	5.06 m		4.25 m		4.44 m	4.32 m
H-3′,H-3, 4H	8.18 m		8.17 m		7.96 m	7.96 m
H-4′,H-4″, 4H	7.37 m		7.34 m		7.39 m	7.40 m
H-5′,H-5″, 2H	7.48 m		7.50 m		7.52 m	7.53 m
-OAc					2.06 s	2.06 s
					2.04 s	2.02 s
					2.03 s	2.02 s

Table 2. ^{13}C NMR of Microcarpin A, B [100MHz,in C_5D_5N, δ(ppm)]

microcarpin A				microcarpin B			
C	δ	C	δ	C	δ	C	δ
1	69.6 t	1′	166.8 s	1	69.1 t	1′	166.7 s
2	70.2 d	1″	167.0 s	2	69.9 d	1″	166.0 s
3	131.9 d	2′	131.1 s	3	135.3 d	2′	131.3 s
4	133.6 d	2″	131.2 s	4	127.8 d	2″	131.0 s
5	73.6 d	3′,3″	130.1 d	5	76.8 d	3′,3″	130.1 d
6	73.8 d	4′,4″	128.9 d	6	74.4 d	4′	128.8 d
7	67.8 t	5′,5″	133.3 d	7	64.0 t	4″	128.9 d
						5′,5″	133.3 d

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