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PHLOROGLUCINOL DERIVATIVES FROM FRUITS OF *MALLOTUS JAPONICUS*

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Key Word Index—*Mallotus japonicus*, Euphorbiaceae, 3-(3, 3-dimethylallyl)-5-(3-acetyl-2, 4-dihydroxy-5-methyl-6-methoxybenzyl)-phloracetophenone, 3-(3-methyl-2-hydroxybut-3-enyl)-5-(3-acetyl-2, 4-dihydroxy-5-methyl-6-methoxybenzyl)-phloracetophenone, ^{1}H NMR, ^{13}C NMR

Abstract—Two new rottlerin-like phloroglucinol derivatives were isolated from the fruits of *Mallotus japonicus* and identified by chemical and spectral data as 3-(3, 3-dimethylallyl)-5-(3-acetyl-2, 4-dihydroxy-5-methyl-6-methoxybenzyl)-phloracetophenone and 3-(3-methyl-2-hydroxybut-3-enyl)-5-(3-acetyl-2, 4-dihydroxy-5-methyl-6-methoxybenzyl)-phloroacetophenone

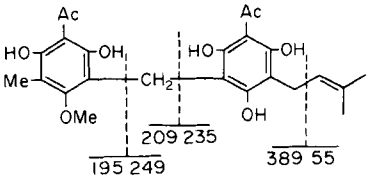
INTRODUCTION

Mallotus japonicus is a deciduous tree widely distributed in Japan Its bark has been used in folk medicine for stomach disorders in Japan and for cancer in Formosa Bergenin was isolated from the bark[1], rutin from the leaves [2], and cardiac glycosides from the seeds [3, 4] The present communication describes the isolation and structure elucidation of phenolic constituents, compounds **A** and **B** obtained from the fruit glands of the plant, the structures (**1** and **2**) of which resemble rottlerin [5] from 'Kamala' (*M philippinensis*)

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum (Table 1) of compound **A**, mp 188–189° indicated the presence of three methyl, two acetyl, one methoxyl, and two methylene groups, but no aromatic proton. Methylation of **A** with diazomethane gave a pentamethyl ether On acetylation it gave a penta-acetate, the ^{1}H NMR spectral data of which are given in Table 1 The mass ion peaks of **A** were found at *m/z* 444 $[M]^+$, 389 $[M-55]^+$, 249, 235, 209 and 195, suggesting a diphenylmethane structure (**1**) like rottlerin [5] for **A** Reductive alkaline cleavage [6] of **A** afforded 2, 6 - dihydroxy - 3 - methyl - 4 - methoxyacetophenone[7, 8], confirming the structure of the corresponding moiety of **A** The remaining part of **A** should include another phloracetophenone with a 3, 3-dimethylallyl group, as indicated by the ^{1}H NMR data (Table 1) Therefore, **A** was deduced as 3-(3, 3-dimethylallyl)-5-(3-acetyl-2, 4-dihydroxy-5-methyl-6-methoxybenzyl)-phloracetophenone (**1**), which was also supported by ^{13}C NMR data (Table 2)

Compound **B**, mp 197–199° and its acetate showed the ^{1}H and ^{13}C NMR spectral data given in Tables 1 and 2 In comparison of these data with those of compound **A** and its acetate it is obvious that the structure of **B** is quite similar to that of **A** except for the side chain structure The elemental analysis of **B** and mass ion peaks at *m/z* 460 $[M]^+$ and 389 $[M-71]^+$ indicated the molecular formula as $C_{24}H_{28}O_9$ and the presence of one more oxygen atom in the side chain of **B** The ^{13}C NMR signal at δ 78 2 (Table 2) and the acetoxy methyl signal at δ 1 93 (Table 1, **B** acetate) indicated the presence of a secondary hydroxyl group in the side chain of **B** Moreover, the proton coupling data suggested a partial structure $-CH_2-CH(OH)-$ and a terminal methylene group in the side chain Therefore, the structure of **B** was deduced as 3-(3-methyl-2-hydroxybut-3-enyl)-5-(3-acetyl-2, 4-dihydroxy-5-methyl-6-methoxybenzyl)-phloracetophenone (**2**) although the stereochemistry of the secondary hydroxyl group remains unresolved



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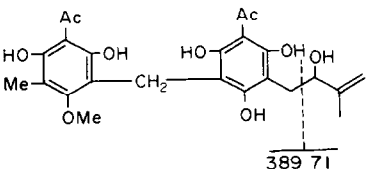

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Table 1 ^{1}H NMR data* of compounds **A**, **B** and their corresponding acetates

Assigned protons	**A**	**B**	**A** acetate	**B** acetate
Me (on ring)	2 12 (3H, *s*)	2 12	2 07†	2 06†
Ac (on ring)	2 68 (3H, *s*)	2 72	2 36	2 36
	2 71 (3H, *s*)	2 72	2 38	2 39
OMe	3 98 (3H, *s*)	3 97	3 60	3 56
CH_2 (between rings)	3 73 (2H, *s*)	3 73	3 71	3 70
CH_2 (in side chain)	3 39 (2H,*d*)[a]	2 68 (1H, *dd*)[b]	3 08 (2H, *d*)[c]	2 55 (1H, *dd*)[d]
		3 16 1H, *dd*)[e]		2 92 (1H, *dd*)[f]
CH (in side chain)	5 19 (1H,*t*)[a]	4 33 (1H, *dd*)[g]	4 95 (1H, *t*)[c]	5 26 (1H, *dd*)[h]
Me (in side chain)	1 79 (3H, *br s*)	1 86 (3H, *s*)	1 67 (6H, *s*)	1 72 (3H,*s*)
	1 84 (3H, *br s*)			
=CH_2(terminal)	—	4 89 (1H, *br s*)	—	4 83 (2H, *br s*)
		5 02 (1H, *br s*)		
OAc (on side chain)	—	—	—	1 93 (3H, *s*)
OAc (on ring)	—	—	2 13†	2 15†
			2 13†	2 16†
			2 18†	2 24
			2 22	2 30
			2 28	2 30

*Chemical shifts are given in δ values relative to TMS in a $CDCl_3$ solution, *s*, singlet, *d*, doublet, *dd*, double doublet, *t*, triplet, *br*, broad

†Assignments are tentative in each vertical column

(a–h) Coupling constants are shown in Hz as follows (a) 6 8, (b) 15 3 and 9 0, (c) 6 3, (d) 14 4 and 5 2, (e) 15 3 and 2 7, (f) 14 4 and 7 2, (g) 9 0 and 2 7, (h) 7 2 and 5 2

Table 2 ^{13}C NMR data* of compounds **A** and **B**

Assigned carbon	**A**		**B**	
Me (on ring)	8 8 *q*		8 8 *q*	
Me (acetyl)	32 6 *q*		32 8 *q*	
	33 6 *q*		33 7 *q*	
CO	204 3 *s*		204 9 *s*	
	205 4 *s*		205 5 *s*	
OMe	61 8 *q*		61 8 *q*	
CH_2 (between rings)	16 9 *t*		17 1 *t*	
Me (in side chain)	17 9 *q*		18 4 *q*	
	25 8 *q*			
=CH_2 (terminal)			110 7 *t*	
=C–	136 9 *s*		146 8 *s*	
|				
=CH–	121 3 *d*			
–CH–OH			78 2 *d*	
|				
CH_2(in side chain)	22 1 *t*		29 3 *t*	
Ring carbon (all singlets)	104 7	157 3	104 9	157 3
	105 3	158 6	105 7	157 3
	105 8	159 6	105 9	159 7
	108 8	159 9	108 9	160 2
	109 0	159 9	109 1	160 5
	109 5	162 4	109 6	162 6

*Chemical shifts are given in δ values relative to TMS in a $CDCl_3$ solution, *q*, quartet, other abbreviations are shown in Table 1

EXPERIMENTAL

Isolation The air-dried capsules (without seeds, 640 g) of *M japonicus* Muell Arg were extracted with MeOH at room temp for 4 days The MeOH filtrate was concd to give ppts, which were crystallized from MeOH to afford yellow needles (compound **A**) The filtrate separated from **A** was evaporated to dryness, dissolved in H_2O and extracted with hexane and then with EtOAc to give a hexane extract (9 7 g) and an EtOAc extract (24 3 g) The latter was purified on a Sephadex LH-20 column ($CHCl_3$–MeOH, 1 1) followed by repeated CC on Si gel (hexane–$CHCl_3$ and then hexane–EtOAc) to afford additional **A** and compound **B**

Compound A Yellow needles (2 4 g) from MeOH, mp 188–189° (uncorr) UV λ_{max}^{EtOH} nm(ϵ) 293 (23 200), IR ν_{max}^{KBr} cm^{-1}, 3310 (OH), 3220, 1615, 1595, 1558, 1434, 1390, 1365, 1260, 1208, 1172, 1128, MS *m/z* 444 $[M]^+$, 389 $[M-55]^+$, 249, 235, 209, 195, 181, NMR Tables 1 and 2 (Found C, 64 35, H, 6 44 $C_{24}H_{28}O_8$ requires C, 64 85, H, 6 35%) *Pentamethyl ether of* **A** A MeOH soln of **A** (14 1 mg) was treated with CH_2N_2–Et_2O The resulting products purified by CC on Si gel gave a colourless oil (4 2 mg), MS *m/z* 514 $[M]^+$, ^1H NMR $\delta(CDCl_3)$ 1 68, 1 75 (3H, *br s* each, Me), 2 15 (3H, *s*, Me), 2 51 (6H, *s*, Ac), 3 31 (2H, *d*, $J = 6$ 2 Hz), 3 46, 3 59 (3H, *s* each, OMe), 3 50, 3 70 (6H, *s* each, OMe), 4 00 (2H, *s*, CH_2 between rings), 5 16 (1H, *t*, $J = 6$ 2 Hz) *Penta-acetate of* **A** **A** (20 mg) was acetylated with Ac_2O (1 ml) and pyridine (1 ml) at room temp for 10 min After usual treatment the resulting products were purified by CC on Si gel **A** colourless oil (15 mg) was obtained, MS *m/z* 654 $[M]^+$, ^1H NMR Table 1

Compound B Yellow needles (88 mg) from MeOH, mp 197–199° (uncorr) UV λ_{max}^{EtOH} nm(ϵ) 232 (22 600), 289 (18 600), 323 (16 400), IR ν_{max}^{KBr} cm^{-1} 3320 (OH), 3230, 1603, 1415, 1362, 1292, 1170, 1128, MS *m/z* 460 $[M]^+$, 417 $[M-43]^+$, 389 $[M-71]^+$, 209, 195, 181, NMR Tables 1 and 2 (Found C, 62 34, H, 6 23 $C_{24}H_{28}O_9$ requires C, 62 60, H, 6 13%) *Hexa-acetate of* **B** Using acetylation as described for **A**, a colourless oil was obtained, MS *m/z* 712 $[M]^+$, ^1H NMR Table 1

Reductive alkaline cleavage of **A** **A** (120 mg) dissolved in 5% NaOH (60 ml) was mixed with Zn powder (0 6 g) and warmed for 5 min at 100° The filtrate of the reaction mixture was acidified with 10% H_2SO_4 and extracted with Et_2O After evaporation of Et_2O the residue was purified through a Si gel column (hexane–EtOAc, 13 5) to afford yellow needles (32 5 mg), mp 197–200° (uncorr) MS *m/z* 196 $[M]^+$, 181, ^1H NMR (CD_3OD) δ 1 91 (3H, *s*, Me), 2 63 (3H, *s*, Ac), 3 81 (3H, *s*, OMe), 6 00 (1H, *s*) It was identified by comparison with an authentic sample of 2, 6-dihydroxy-3-methyl-4-methoxyacetophenone [6] by mmp and comparison of spectral data

Acknowledgement—We wish to thank Professor S Matsuura, Gifu Pharmaceutical Collage for an authentic sample of 2, 6-dihydroxy-3-methyl-4-methoxyacetophenone

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CANDIDOL, A FLAVONOL FROM *TEPHROSIA CANDIDA*

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Key Word Index—*Tephrosia candida*, Leguminosae, flavonol, candidol, 3,4'-dihydroxy-5,6,7-trimethoxyflavone

Abstract—The seeds of *Tephrosia candida* have yielded a new flavonol, characterized here as 3,4'-dihydroxy-5,6,7-trimethoxyflavone

Earlier investigations [1, 2, Chibber, S S and Dutt, S K , unpublished] of the seeds of *Tephrosia candida* have revealed the presence of three new flavonoids We report here the isolation and characterization of a flavonol, candidol, from the ethyl acetate extract of the seeds It analysed for $C_{18}H_{16}O_7$ and produced a yellow fluorescence in UV light It responded to Shinoda's test for flavonoids giving a magenta colour