Phytochemistry, Vol. 24, No. 3, pp. 620–621, 1985.
Printed in Great Britain.

0031-9422/85 $3.00 + 0.00

FURTHER PHLOROGLUCINOL DERIVATIVES IN THE FRUITS OF *MALLOTUS JAPONICUS*

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(*Received* 24 *April* 1984)

Key Word Index—*Mallotus japonicus*; Euphorbiaceae; 2,6-dihydroxy-3-methyl-4-methoxyacetophenone; 3-(3,3-dimethylallyl)-5-(3-acetyl-2,4-dihydroxy-5-methyl-6-methoxybenzyl)-phlorobutyrophenone; 3-(3,3-dimethylallyl)-5-(3-acetyl-2,4-dihydroxy-5-methyl-6-methoxybenzyl)-phloroisobutyrophenone.

Abstract—Two new rottlerin-like phloroglucinol derivatives were detected from the fruits of *Mallotus japonicus* and identified as 3-(3,3-dimethylallyl)-5-(3-acetyl-2,4-dihydroxy-5-methyl-6-methoxybenzyl)-phlorobutyrophenone and -phloroisobutyrophenone by spectral studies. 2,6-Dihydroxy-3-methyl-4-methoxyacetophenone was also isolated.

Recently, we reported [1] two new rottlerin-like compounds, A and B, from the fruits of *Mallotus japonicus*. Further studies on the same fruits have now added two more compounds, C and D. Compound C was identified as 2,6-dihydroxy-3-methyl 4-methoxyacetophenone [2], and is a moiety of compound A. The ^{1}H NMR and ^{13}C NMR spectra (Tables 1 and 2) of compound D are quite similar to those of A except for some signals due to acyl groups. The mass spectrum of D showed a molecular ion of *m/z* 472, 28 more than A, suggesting two more carbons than A. The NMR signals due to the acyl proton and carbons (Tables 1 and 2) indicated that compound D was still a mixture. However, it was difficult to isolate the pure components from D itself. The pentaacetate of D could be separated by HPLC to give two pentaacetates, Da and Db. The ^{1}H NMR data of the two acetates are also given in Table 1, showing that the structure of Da bears a propyl ketone group and Db an isopropyl ketone group instead of one of two acetyl groups of A. The proton signals of the propyl and isopropyl groups were confirmed by ^{1}H decoupling techniques to each other. The ^{13}C NMR spectral data (Table 2) are also consistent with the structures. Since the mass spectrum of D showed strong signals of *m/z* 195 and 209, similar to the case of A, a propyl or an isopropyl group must be located on the phloroglucinol nucleus which bears the isopentenyl group.

EXPERIMENTAL

The air-dried capsules (without seeds, 1.4 kg) of *M. japonicus* were extracted twice with H_2O overnight to remove H_2O-soluble ingredients and washed with H_2O. The air-dried material was then extracted with MeOH at room temp. and the MeOH filtrate was concd to give a ppt. (27 g, compound A). The filtrate separated from A was evapd to give a dry extract (164 g), 25 g of which was dissolved in H_2O and purified on a Sephadex LH-20

Table 1. ^{1}H NMR spectral data of compounds Da and Db ($CDCl_3$)

Assigned protons	Da	Db	Da acetate	Db acetate
Me (on ring)	2.12	2.12	2.06	2.07
Ac (on ring)	2.72	2.72	2.38	2.36
OMe	3.97	3.97	3.59	3.59
CH_2 (between rings)	3.73	3.73	3.69	3.69
CH_2 (in side chain)	3.39	3.39	3.07	3.06
(2H, *br d*)	(*J* = 7.5 Hz)		(*J* = 5.7 Hz)	
CH (in side chain)	5.18	5.18	4.96	4.98
Me (in side chain)	1.79	1.79	1.67 (6H, *s*)	1.65
	1.84	1.84		1.67
Me (in acyl group)	0.99 (3H) (*t*, *J* = 7.5 Hz)	1.18 (6H) (*d*, *J* = 7.1 Hz)	0.92 (3H) (*t*, *J* = 7.9 Hz)	1.10 (6H) (*d*, *J* = 6.8 Hz)
CH_2 (in acyl group)	1.70 *m*		1.62 *m*	
	3.07 *t* (*J* = 7.5 Hz)		2.62 *t* (*J* = 7.9 Hz)	
CH (in acyl group)		3.95 *m*		3.50 *m*

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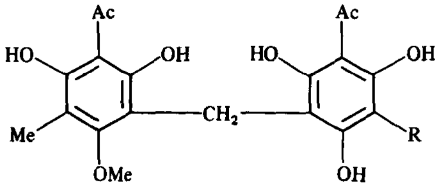
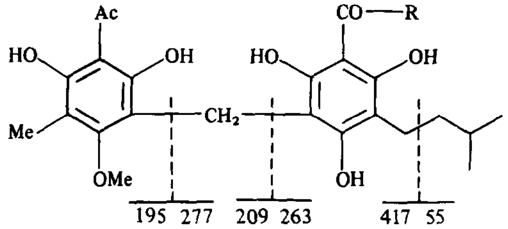
Table 2. ^{13}C NMR spectral data of compounds A, Da and Db (in ppm)

Assigned carbons	A	Da	Db
Me (on ring)	8.8	8.8	8.8
Me (in acetyl)	33.6	33.7	33.7
CO	204.3	205.5	205.5
	205.4	207.0	207.0
OMe	61.8	61.8	61.8
CH_2 (between rings)	16.9	17.0	17.0
Me (in side chain)	17.9	18.0	18.0
	25.8	25.8	25.8
CH_2 (in side chain)	22.1	22.1	22.1
CH (in side chain)	121.3	121.4	121.4
C (in side chain)	136.9	136.9	136.9
Me (in acyl group)	32.6	14.0	18.0
			19.3
CH_2 and CH (in acyl group)		17.0*t* 45.8*t*	39.2d



A R = $CH_2CH = CMe_2$
B R = $CH_2CHOHC(Me) = CH_2$



Da R = CH_2CH_2Me
Db R = $CHMe_2$

column (MeOH) followed by repeated CC on silica gel (hexane–EtOAc, 3:2) to afford compounds C (15.4 mg) and D (274 mg).

Compound C. Yellow needles from $CHCl_3$, mp 200–201° (uncorr.). MS *m/z*: 196 $[M]^+$ and 181; ^1H NMR ($CDCl_3$): δ2.01 (3H, *s*, Me), 2.68 (3H, *s*, Ac), 3.83 (3H, *s*, OMe), 5.95 (1H, *s*), 9.35 (1H, *br s*, OH), and 9.70 (1H, *br s*, OH). It was identical (mmp, IR and ^1H NMR) with an authentic sample of 2,6-dihydroxy-3-methyl-4-methoxyacetophenone.

Compound D. Yellow needles from hexane–EtOAc, mp 157–158° (uncorr.). MS *m/z*: 472 $[M]^+$, 417, 277, 209 and 195; IR ν_{max}^{nujol} cm^{-1}: 3250 (OH), 1625 sh (CO) and 1608 (CO); ^1H NMR and ^{13}C NMR see Tables 1 and 2; the integrated areas of the two methyl signals at 0.99 (3H, *t*) and 1.18 (6H, *d*) ppm are almost the same, indicating a mixture of Da and Db (2:1).

Pentaacetate of D. D (30 mg) was acetylated with Ac_2O (1 ml) and pyridine (1 ml) at room temp. for 1 hr. After usual treatment, the resulting products were purified by HPLC (Finepak SIL column, 4.6 mm i.d. × 250 mm, at a flow rate of 1 ml $CHCl_3$/min) to give Da acetate (10 mg, t_R 9.5 min) and Db acetate (4 mg, t_R 11.5 min). MS *m/z*: 682 $[M]^+$; ^1H NMR: see Table 1.

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

REFERENCES

1. Shigematsu, N., Kouno, I. and Kawano, N. (1983) *Phytochemistry* **22**, 323.
2. Matsuura, S. (1957) *Yakugaku Zasshi* 77, 302.