Isolation and Characterisation of Bergenin Derivatives from *Macaranga peltata*

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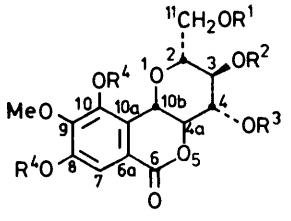
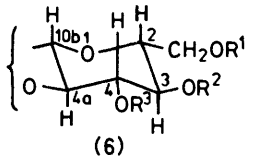
The isolation of bergenin and three *O*-methyl ethers of bergenin from *Macaranga peltata* is reported, and the ^1H and ^{13}C n.m.r. spectra of bergenin and its derivatives are discussed.

Macaranga peltata Muell [syn: *Macaranga roxburghi* (Euphorbiaceae)] is a small tree commonly found in Indian forests.[1] The gum-powder from *Macaranga peltata* has been used in Indian medicine for the treatment of venereal diseases.[2] Of the *Macaranga* genus, only *M. tenarus* has been previously examined and the isolation of a new diterpene, macaranganol, and some other terpenoids was reported.[3]

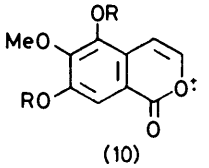
In the present investigation extraction of the heartwood of *Macaranga peltata* gave a red gummy residue from which bergenin and β-sitosterol were isolated.



(1) $R^1=R^2=R^3=R^4=H$
(2) $R^1=R^2=R^3=H, R^4=Me$
(3) $R^1=R^4=Me, R^2=R^3=H$
(4) $R^1=R^3=H, R^2=R^4=Me$
(5) $R^1=R^2=R^3=R^4=Ac$
(7) $R^1=R^2=R^3=Ac, R^4=Me$
(8) $R^1=R^4=Me, R^2=R^3=Ac$
(9) $R^1=R^3=Ac, R^2=R^4=Me$
(13) $R^1=R^2=R^3=R^4=Me$

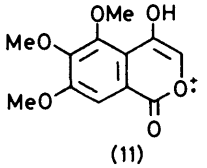


(6)



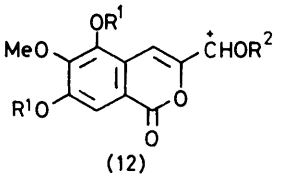
(10)

a; R = H (*m/e* 208)
b; R = Me (*m/e* 236)
c; R = Ac (*m/e* 292)



(11)

(*m/e* 252)



(12)

a; $R^1=Me, R^2=H$ (*m/e* 265)
b; $R^1=Me, R^2=Ac$ (*m/e* 307)
c; $R^1=R^2=Ac$ (*m/e* 363)
d; $R^1=Ac, R^2=H$ (*m/e* 321)
e; $R^1=R^2=Me$ (*m/e* 279)

Bergenin (1) is a crystalline compound which has been previously isolated from several species.[4-21] However, this paper reports for the first time its isolation from *M. peltata*. Furthermore, extraction of the bark of *M. peltata* gave, in addition to bergenin, the 8,10-di-*O*-methyl ether (2), and two tri-*O*-methyl ethers, which have been shown to have structures (3) and (4) respectively.

The ^1H and ^{13}C n.m.r. spectra of bergenin fully support the revised structure (1) proposed independently by Hay and Haynes [22] and Posternak and Durr.[23] The ^1H n.m.r. spectrum (Table 1) shows only one aromatic proton at τ 2.98 and a singlet due to the methoxy-group at τ 6.18. In addition there is a one-proton doublet at τ 5.11 (J 10 Hz) due to the benzylic hydrogen and it can be deduced that there are no hydrogen-bonded hydroxy-groups since there are no signals below τ 0.

The spectrum of the penta-acetate (5) was particularly useful. By comparison with the spectrum of the unacetylated material it can be seen that the benzylic proton has hardly moved and is therefore not attached to a hydroxy-group. However, two signals have moved downfield on acetylation and now appear as triplets (coupled to each other) at τ 4.53 and 4.91. The lower triplet is also coupled to a triplet at τ 5.68, whilst the triplet at τ 4.91 is coupled to a multiplet at τ 6.21 which has not moved on acetylation and is therefore due to a >CHOR group. The protons of the methylene group appear as double doublets at τ 5.69 and 5.89, each coupled to the multiplet at τ 6.21. A six-carbon aliphatic system is therefore established and the large coupling constants (10 Hz) suggest that the methine protons are all *trans* and diaxial as in (6). To account for the chemical shift of the aromatic proton in bergenin and its derivatives it must clearly be *ortho* to the carbonyl group.[24]

The ^{13}C n.m.r. spectrum of bergenin (Table 2) contains a signal at 163.38 p.p.m., readily attributable to the ester carbonyl carbon atom, and three other low field signals due to the oxygenated aromatic carbon atoms. One aromatic carbon atom at 109.80 p.p.m. is clearly distinguished as a doublet in the off-resonance spectrum. The chemical shift of this signal in the spectrum of bergenin and its dimethyl ether (2), and its shift upon acetylation, unambiguously confirm the positions of the hydroxy- and methoxy-groups attached to the dihydroisocoumarin moiety.

TABLE 1

^{1}H N.m.r. spectra of bergenin and its derivatives *

Proton	Bergenin (1) $CDCl_3$–DMSO (1 : 1)	Penta-acetate (5) $CDCl_3$	8,10-Di-*O*-methyl ether (2) $CDCl_3$–DMSO (1 : 1)	Triacetate (7) $CDCl_3$	8,10,11-Tri-*O*-methyl ether (3) $CDCl_3$	Diacetate (8) $CDCl_3$	3,8,10-Tri-*O*-methyl ether (4) $CDCl_3$–DMSO (1 : 1)	Diacetate (9) $CDCl_3$	Pentamethyl ether (13) $CDCl_3$
CH_2	5.9—6.9 (6 H)	5.69(dd, 13, 2) 5.89(dd, 13, 4)	6.0—6.7 (6 H)	5.73(d, 3)	5.8—6.4 (6 H)	6.40(m)	5.9—6.9 (6 H)	5.43(dd, 12, 2) 5.72(dd, 12, 5)	5.8—6.9 (6 H)
2		6.21(m)		6.1(m)		6.15(m)		6.2(m)	
3		4.91(t, 10)		4.89(t, 10)		4.84(t, 10)		6.62(dd, 8, 10)	
4		4.53(t, 10)		4.49(t, 10)		4.46(t, 10)		4.46(dd, 8, 10)	
4a		5.68(t, 10)		5.71(t, 10)		5.70(t, 10)		5.82(t, 10)	
10b	5.11(d, 10)	5.19(d, 10)	5.30(d, 10)	5.18(d, 10)	5.26(d, 10)	5.16(d, 10)	5.28(d, 10)	5.20(d, 10)	5.37(d, 10)
7	2.98(s)	2.25(s)	2.66(s)	2.55(s)	2.59(s)	2.53(s)	2.63(s)	2.54(s)	2.57(s)
OH	4.5br (2 H) 5.9—6.9 (3 H)		4.48(d, 4) 4.85br(d, 4) 5.74br(t, 5)		5.8—6.4 (2 H)		4.27(d, 5) 5.50(dd, 5, 7)		
OMe	6.18(s)	6.14(s)	6.15(s) 6.16(s) 6.19(s)	6.07(s) 6.10(s) 6.16(s)	6.08(s) 6.13(s) 6.16(s) 6.58(s)	6.03(s) 6.07(s) 6.10(s) 6.60(s)	6.12(s) 6.13(s) 6.17(s) 6.43(s)	6.04(s) 6.08(s) 6.15(s) 6.51(s)	6.09(s) 6.11(s) 6.14(s) 6.27(s) 6.43(s) 6.59(s)
OAc		7.70(s, ×2) 7.93(s, ×2) 7.97(s)		7.91(s) 7.92(s) 7.96(s)		7.88(s) 7.92(s)		7.80(s) 7.88(s)	

* Chemical shifts are given in τ, coupling constants (in Hz) are in parentheses. Assignments are supported by appropriate spin-decoupling experiments and correct integration.

TABLE 2

^{13}C N.m.r. spectra of bergenin and its derivatives *

Carbon	Bergenin (1) $CDCl_3$–DMSO (1 : 1)	Penta-acetate (5) $CDCl_3$	8,10-Di-*O*-methyl ether (2) $CDCl_3$–DMSO (1 : 1)	Triacetate (7) $CDCl_3$	8,10,11-Tri-*O*-methyl ether (3) $CDCl_3$	Pentamethyl ether (13) $CDCl_3$
CH_2	61.26	61.79	61.25	62.55	72.44	71.58
2	70.66	68.21	70.45	69.03	71.07	72.22
3	72.58	72.08	71.50	72.43	72.00	79.45 (×2)
4	73.87	72.69	74.07	72.57	74.66	80.60
4a	79.76	76.57 (×2)	80.26	76.60	79.16	84.79
10b	81.72		81.40	77.10	80.05	
10a	115.63	129.43	119.10	118.90	118.86	119.13
10	147.97	141.19	151.11	151.41	151.40	151.45
9	140.64	149.82	148.06	149.02	148.94	148.70
8	150.87	143.98	153.13	154.12	153.69	153.73
7	109.80	123.82	109.19	110.05	109.83	109.67
6a	117.91	118.52	126.46	125.06	126.28	126.16
6	163.38	161.37	163.70	163.10	164.49	163.90
OMe	59.92	61.39	56.00 60.68 61.25	56.32 61.07 61.73	56.25 59.43 61.08 61.66	56.22 59.21 60.76 61.01 61.10 61.57
OAc		20.52 (×3) 20.67 (×2) 167.41 167.98 169.36 169.70 170.17		20.64 20.73 20.79 169.76 170.15 170.56		

* Measurements are given as p.p.m. downfield from tetramethylsilane. All assignments are supported by off-resonance decoupling experiments.

In the ^{1}H n.m.r. spectrum of the di-*O*-methyl ether (2) the three methoxy-groups give singlets at τ 6.15, 6.16, and 6.19 while the three hydroxy-groups come at τ 4.48, 4.85, and 5.74 (Table 1). The spectrum of the corresponding triacetate (7) closely resembles that of the penta-acetate (5) apart from the obvious differences in the numbers of methoxy- and acetoxy-signals.

The two tri-*O*-methyl ethers (3) and (4) showed very

similar ^{1}H n.m.r. spectra each having one methoxy group at high field. However, the spectra of the corresponding diacetates (8) and (9) showed significant differences which could be used to locate the extra *O*-methyl group in each case. Thus by comparing the spectrum of (8) with that of (7) and (5) it can be seen that the signals due to 7-, 10b-, 4a-, 4-, 3-, and 2-H are essentially unchanged while the signals due to the CH_2 group are markedly different indicating that this position carries an OMe group in (3) and therefore is not acetylated in (8). Structure (3) is confirmed by the ^{13}C n.m.r. spectrum of this compound in which the signal due to the CH_2 group appears appreciably downfield relative to its position in the spectra of (1) and (2) (Table 2). In a similar way the ^{1}H n.m.r. spectrum of the diacetate (9) derived from (4) clearly shows that in this case the extra *O*-methyl group is located at position 3.

These conclusions were confirmed by periodate oxidation experiments. Thus, while compounds (1)—(3) each consumed approximately one equivalent of periodate, the 3,8,10-tri-*O*-methyl ether (4) did not consume any periodate even after 24 h.

The mass spectra (see Experimental section) of bergenin (1) and its dimethyl ether (2) both show a prominent peak due to the molecular ion and also major peaks corresponding to the fragment ions (10a and b) respectively. Furthermore, the penta-acetate (5) and the triacetate (7) both give a strong peak corresponding to the ion (10c). The mass spectra of the trimethyl ethers (3) and (4) and their corresponding diacetates (8) and (9) were very similar and were therefore of little help in differentiation. However, the presence of strong peaks at *m/e* 265 in the spectra of (3) and (4), and *m/e* 307 in the spectra of (8) and (9), corresponding to (12a and b), respectively, confirm that the extra *O*-methyl group is not attached to C-4 in either compound. In contrast, the mass spectrum of the pentamethyl ether (13), obtained by permethylation of (1) or (4), showed an intense peak at *m/e* 279, corresponding to (12e).

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 237 spectrophotometer and u.v. spectra on a Beckman DB-G spectrophotometer. ^{1}H and ^{13}C n.m.r. spectra were recorded on Varian HA-100 and XL-100 instruments and mass spectra on an AEI MS 9 double-focusing spectrometer. The wood samples were collected from the hills of the Anantagiri forest area, 50 km from Visakhapatnam.

Examination of M. peltata *Heartwood*.—The dry powdered heartwood (1 kg) was successively extracted with hexane (5 l) and methanol (5 l) using a Soxhlet apparatus. The hexane extract on concentration *in vacuo* furnished a pale yellow viscous oil (10 g). Waxes were removed using hot alcohol and the wax-free residue concentrated *in vacuo* to give a pale yellow oil (5 g) which was placed on a column of silica gel (100 g). The column was eluted with hexane, hexane–benzene (1 : 1), and benzene. The hexane fractions (10 × 250 ml) yielded no crystalline compounds and gave only oils (3 g). The hexane–benzene (6 × 250 ml) and benzene (8 × 250 ml) fractions gave β-sitosterol which crystallised from methanol as shining needles (500 mg), m.p. 136—137° (lit.,[25] 134°); acetate (Ac_2O–pyridine at 100°), m.p. 126°.

The methanol extract was freed from tannins by treatment with lead acetate and the tannin-free extract concentrated to give a reddish-brown gum (10 g).

Purification and Identification of Bergenin (1).—Repeated crystallisation of the reddish brown gum from methanol gave shining needles (4.5 g). The crystals readily dissolved in aqueous sodium hydroxide giving a deep yellow solution from which they were regenerated upon acidification, m.p. 150—152°. The compound was thoroughly dried in vacuum for 6 h at 100° to give bergenin, m.p. 237° (lit.,[20] 238°), R_F 0.67 ($CHCl_3$–MeOH 4 : 1) $\lambda_{max.}$(EtOH) 277 nm (log ε 3.98), no shift observed with either NaOAc or boric acid, $\nu_{max.}$(Nujol) 3 380, 3 200br (OH), 1 701, 1 600, 960, and 850 cm^{-1} (Found: C, 51.25; H, 4.9. $C_{14}H_{16}O_9$ requires C, 51.25; H, 4.9%), *m/e* 328.0794 ($C_{14}H_{16}O_9$) and 208.0372 ($C_{10}H_{16}O_5$).

Bergenin Acetate (5).—Bergenin (200 mg) was dissolved in Ac_2O (10 ml) and dry pyridine (2 ml), heated on a water-bath for 6 h, and worked-up in the usual manner. The acetate (150 mg) crystallised from benzene, m.p. 201° (lit.,[20] 207°), R_F 0.59 (C_6H_6–EtOAc 3 : 2), $\lambda_{max.}$(EtOH) 255 (log 3.98) and 210 nm (4.35), $\nu_{max.}$(Nujol) 1 777, 1 740, 1 600, 960, and 890 cm^{-1} (Found: C, 53.55; H, 4.85. $C_{24}H_{26}O_{14}$ requires C, 53.55, H, 4.85%), *m/e* 496 (64%), 454 (88), 418 (29), 405 (31), 376 (54), 363 (67), 334 (42), 321 (51), 293 (24), 292 (95), 279 (57), 274 (100), 261 (40), 259 (37), 250 (43), 237 (29), 236 (18), 224 (42), 221 (24), and 208 (76), *m/e* 496.1217 ($C_{22}H_{12}O_{13}$), 363.0716 ($C_{17}H_{15}O_9$), 321.0610 ($C_{15}H_{13}O_8$), and 292.0583 ($C_{14}H_{12}O_7$).

Examination of M. peltata *Bark*.—The dry powdered bark (4.5 kg) was successively extracted with hexane and methanol using a Soxhlet apparatus. Concentration of the hexane extract gave a residue which resisted crystallisation. It was chromatographed over a column of silica gel and eluted with hexane. The first five fractions (400 ml) gave only waxes which were not investigated further. The next eight fractions gave a compound (1.2 g) which crystallised from chloroform–light petroleum to give shining needles, m.p. 258—259°, $[\alpha]_D^{30}$ −29.0° (chloroform, *c* 1.0), R_F 0.45 (benzene), $\nu_{max.}$ 1 712 (C=O) cm^{-1}. It gave an oxime, m.p. 290—291° and a 2,4-dinitrophenylhydrazone, m.p. 290°. The compound was identified as friedelin (lit.,[26] m.p. 261—265°) by comparison with an authentic sample (mixed m.p. and i.r.).

Further elution of the column with hexane–benzene (4 : 1) gave β-sitosterol (800 mg), m.p. 134—135° (lit.,[25] 134°), $[\alpha]_D^{30}$ −36.5° (chloroform, *c* 1.0), acetate, m.p. 126—127°, identified by comparison with an authentic sample.

The methanol extract was freed from tannins by treatment with lead acetate and the tannin-free extract concentrated to give a pale yellow gum (3.5 g). The gum was chromatographed over silica gel and eluted with chloroform–methanol mixtures. The chloroform–methanol (9 : 1) fractions (10 × 250 ml) yielded a mixture of three compounds which were separated by crystallisation and further chromatography (see below). The chloroform–methanol (3 : 1) fractions (7 × 250 ml) furnished a crystalline compound which was found to be identifical with bergenin.

Purification and Identification of Bergenin Di-O-methyl Ether (2).—The above mixture, on crystallisation from methanol, afforded bergenin di-*O*-methyl ether (2) (600 mg), m.p. 195° (lit.,[20] 196°), R_F 0.2 ($CHCl_3$–MeOH 9.5 : 0.5),

$\nu_{max.}$(KBr) 3 400br, 1 730, 1 710, and 1 600 cm^{-1}, $\lambda_{max.}$(EtOH) 270 (log ε 3.80) and 220 nm (4.40) (Found: C, 53.9; H, 5.65. $C_{16}H_{20}O_9$ requires C, 53.95; H, 5.6%), *m/e* 356 (100%), 265 (11), 252 (16), 239 (24), 238 (20), 237 (65), 236 (72), 224 (18), 223 (62), 221 (19), and 208 (15), *m/e* 356.1 107 ($C_{16}H_{20}O_9$), 265.0 712 ($C_{13}H_{13}O_6$), 252.0634 ($C_{12}H_{12}O_6$), and 236.0685 ($C_{12}H_{12}O_5$). The spectra and physical data for this compound were identical with those of a sample prepared by treating bergenin (200 mg) in methanol (100 ml) at 0° with an ethereal solution of diazomethane (50 ml).

Bergenin Di-O-methyl Ether Triacetate (7).—Acetylation of the di-*O*-methyl ether (2) using pyridine–acetic anhydride at room temperature afforded the acetate, which was recrystallised from methanol, m.p. 130°, $\nu_{max.}$(KBr) 1 740 and 1 600 cm^{-1}, *m/e* 482 (5%), 349 (30), 320 (19), 307 (100), 252 (54), 237 (27), 236 (24), and 223 (25), *m/e* 482.1424 ($C_{22}H_{26}O_{12}$).

Purification and Identification of the Bergenin Tri-O-methyl ethers (3) *and* (4).—The mother-liquor from the crystallisation of (2) was rechromatographed over silica gel and eluted with chloroform–methanol mixtures. The chloroform–methanol (99 : 1) fractions (10 × 100 ml) afforded the 3,8,10-tri-*O*-methyl ether (4) (150 mg) which crystallised from methanol as shining needles, m.p. 258°, R_F 0.45 ($CHCl_3$–MeOH 9.5 : 0.5), *m/e* 370 (32%), 292 (19), 265 (9), 252 (49), 239 (29), 238 (17), 237 (100), 236 (45), 223 (23), 221 (13), and 208 (12), *m/e* 370.1 264 ($C_{17}H_{22}O_9$), 265.0712 ($C_{13}H_{13}O_6$), 252.0634 ($C_{12}H_{12}O_6$), and 236.0685 ($C_{12}H_{12}O_5$).

The chloroform–methanol (98 : 2) fractions (4 × 100 ml) afforded the 8,10,11-tri-*O*-methyl ether (3) (35 mg) which crystallised from dry acetone, m.p. 176°, R_F 0.42 ($CHCl_3$–MeOH 9.5 : 0.5), $\nu_{max.}$(KBr) 3 360br, 1 730, 1 710, and 1 600 cm^{-1}, *m/e* 370 (100%), 265 (18), 252 (19), 239 (27), 238 (21), 237 (91), 236 (63), 224 (11), 223 (44), 221 (18), and 208 (11).

Diacetates (8) *and* (9) *of Bergenin Tri-O-methyl Ethers.*—Acetylation of the 3,8,10-tri-*O*-methyl ether (4) using pyridine and acetic anhydride at room temperature afforded the corresponding diacetate (9) as a semisolid gum, R_F 0.9 ($CHCl_3$–MeOH 9.5 : 0.5), *m/e* 454 (18%), 349 (34), 321 (13), 320 (11), 307 (95), 281 (24), 265 (14), 252 (41), 239 (14), 237 (62), 236 (100), 223 (38), 221 (19), and 208 (12), *m/e* 454.1475 ($C_{21}H_{26}O_{11}$), 307.0818 ($C_{15}H_{15}O_7$), 252.0634 ($C_{12}H_{12}O_6$), and 236.0685 ($C_{12}H_{12}O_5$). Acetylation of the 8,10,11-tri-*O*-methyl ether (3), similarly afforded the diacetate (8), *m/e* 454 (4), 349 (13), 307 (100), 281 (12), 252 (56), 239 (14), 237 (26), 236 (25), 223 (14), and 221 (10).

Periodate Oxidation.—Bergenin (200 mg) was mixed with 0.1N-$NaIO_4$ (20 ml) and the volume made up to 100 ml with distilled water. The solution was set aside at room temperature for 24 h. Excess of periodate was titrated with sodium arsenite solution (0.04N). Bergenin consumed 1.13 equivalents of periodate, while on similar oxidation the 8,10-di-*O*-methyl ether (2) consumed 0.91 equivalents and the 8,10,11-tri-*O*-methyl ether (3) consumed 0.86 equivalents. The 3,8,10-tri-*O*-methyl ether did not consume any periodate even after standing for 24 h.

Bergenin Pentamethyl Ether (13).—To a solution of bergenin (100 mg) in dimethylformamide (DMF) (5.0 ml), methyl iodide (1.5 ml), and freshly precipitated Ag_2O (1.5 g) were added in small portions during 1 h and shaken at room temperature for 24 h. The contents were filtered and the residue washed with DMF (5.0 ml). The combined filtrate was shaken with chloroform (20 ml) and the chloroform layer washed with a dilute solution of KCN (5 × 10 ml) followed by water. The dried chloroform layer on evaporation under reduced pressure gave a solid (50 mg) which could be crystallised from ether–light petroleum, m.p. 105° (Found: C, 57.4; H, 6.8. $C_{19}H_{26}O_9$ requires C, 57.3; H, 6.6%), *m/e* 398 (15%), 310 (12), 296 (43), 279 (21), 269 (13), 253 (11), 251 (13), 239 (41), 237 (51), 236 (27), 223 (21), 221 (13), 115 (100), and 101 (44).

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