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ON THE CHEMISTRY OF INDIAN ORCHIDACEAE PLANTS—II†

DENGIBSIN AND DENGIBSININ, THE FIRST NATURAL FLUORENONE DERIVATIVES FROM *DENDROBIUM GIBSONII* LINDL.

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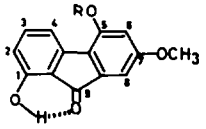
Abstract—*Dendrobium gibsonii*, an Orchidaceae plant yielded the first natural fluorenone derivatives designated dengibsin and dengibsinin to which 1,5-dihydroxy-7-methoxy-9-fluorenone (**1**) and 1,6-dihydroxy-5,7-dimethoxy-9-fluorenone (**2**) structures have been assigned respectively. The structures are fully supported by the ^{1}H-NMR, IR, UV and MS spectral data of dengibsin and dengibsinin and a number of their pertinent derivatives. Aurantiamide acetate, dimethyl terephthalate and β-sitosterol have been isolated as the other constituents.

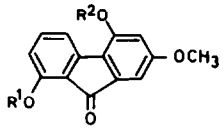
In continuation of our earlier studies on the chemistry of Indian Orchidaceae,[1] we now report on the structure elucidation of the two new isolates of *Dendrobium gibsonii* Lindl., designated dengibsin and dengibsinin which are shown to possess 1,5-dihydroxy-7-methoxy-9-fluorenone (**1**) and 1,6-dihydroxy-5,7-dimethoxy-9-fluorenone (**2**) structures respectively on the basis of the spectral properties, specially the ^{1}H-NMR data of the parent compounds and some of their pertinent derivatives. To our knowledge, the isolation of **1** and **2** constitutes the first report of the natural occurrence of fluorenone derivatives. The other isolates were characterised as the modified dipeptide aurantiamide acetate (**16**), dimethyl terephthalate and the ubiquitous β-sitosterol.

Dendrobium gibsonii, an epiphytic herb growing in Sikkim Himalaya, Assam, Khasia mountains and Burma,[2] was collected for the present investigation from Darjeeling district, W. Bengal, India, at an altitude of 2500 m. It possesses slender stems with lanceolate acuminate leaves and tubular basal sheaths and grows yellow to orange flowers.

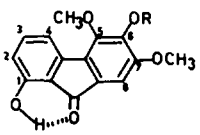
Dengibsin (**1**), $C_{14}H_{10}O_4$ (M^+ 242), m.p. 227°, $[\alpha]_D$ ±0°, isolated as deep red needles from the $CHCl_3$ extract of the whole orchid *D. gibsonii* exhibited IR (KBr) absorptions indicative of phenolic OH ($FeCl_3$ colour positive) chelated with conjugated C=O group (3330 and 1715 cm^{-1}). It formed two methyl ethers, *viz*, monomethyl ether (**4**) and dimethyl ether (**5**) and two acetates, *viz*, monoacetate (**6**) and diacetate (**7**) (*vide*



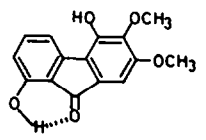
(1) R = H
(4) R = CH_3
(6) R = $COCH_3$



(5) $R^1 = R^2 = CH_3$
(7) $R^1 = R^2 = COCH_3$



(2) R = H
(9) R = CH_3
(12) R = $COCH_3$



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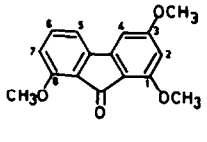

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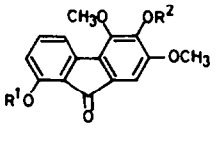
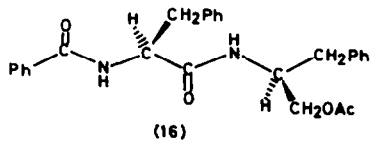


(10) $R^1 = CH_3$, $R^2 = H$
(11) $R^1 = R^2 = CH_3$
(13) $R^1 = R^2 = COCH_3$
(14) $R^1 = COCH_3$, $R^2 = CH_3$
(15) $R^1 = CH_3$, $R^2 = COCH_3$



(16)

† For Part I see Ref. 1.

Experimental) indicating thereby the presence of one free and one chelated phenolic OH groups in the molecule. The UV and visible spectrum of **1** exhibits a pattern similar to that of fluorenone (Table 1) and hence suggesting **1** to be a fluorenone derivative. The ^{1}H-NMR spectrum (100 MHz, d_6-acetone) exhibits signals for one aromatic OMe (δ 4.08, 3H, s), one chelated phenolic OH (δ 8.92, 1H, s, disappeared on D_2O shake), two *meta*-coupled aromatic protons (δ 6.77 and 6.82, each 1H, d, J = 1.7 Hz) and three other aromatic protons (δ 6.9–7.2, 3H, m). A comparative study on the ^{1}H-NMR spectra of dengibsin, its monoacetate, and its diacetate (Table 2) reveals that one *meta*-coupled (d, J = 1.7 Hz) aromatic proton suffers significant downfield shift on acetylation of the free phenolic OH group and another *ortho*- and *meta*-coupled aromatic proton (dd, J = 7.5 and 1.5 Hz) on acetylation of the chelated phenolic OH group. Therefore, dengibsin is a dihydroxymonomethoxy fluorenone derivative in which one benzene ring contains the *meta*-coupled aromatic protons and the OMe and free OH groups while the other ring contains the remaining three aromatic protons and the chelated OH group. Since only one of the *meta*-coupled aromatic protons is deshielded on acetylation of the free phenolic OH group dengibsin can be assigned the structure **1**. Furthermore, the dimethyl ether of dengibsin was found to be different from 1,3,8-trimethoxyfluorenone (**8**), recently synthesised by Nakano *et al.*[3] From this nonidentity the presence of the oxygen functions at 1,5,7 and not 1,3,8 (≡ 1,6,8 of structure **1**) is immediately obvious.

Dengibsinin (**2**), $C_{15}H_{12}O_5$ (M^+ 272), m.p. 220°, $[\alpha]_D$ ±0°, isolated as orange–red needles from both the petrol and chloroform extracts, gave positive $FeCl_3$ colouration and exhibited IR (KBr) absorption bands (3290 and 1715 cm^{-1}) similar to those of **1**. Its 6-methyl ether (**9**), 1-methyl ether (**10**), 1,6-dimethyl ether (**11**), 6-acetate (**12**), 1,6-diacetate (**13**), 1-acetate-6-methyl ether (**14**) and 6-acetate-1-methyl ether (**15**) were prepared (*vide* Experimental). The UV and visible spectral pattern of **13** is reminiscent of that of fluorenone skeleton (Table 1). The ^{1}H-NMR spectrum (200 MHz, $CDCl_3$) of dengibsinin (**2**) (Table 3) shows the presence of two aromatic OMe (δ 4.14 and 3.96, each 3H, s), one free phenolic OH (δ 6.12, 1H, s, exchangeable with D_2O), one chelated phenolic OH (δ 9.14, 1H, s, disappeared on D_2O shake) and four aromatic protons (δ 7.10, 1H, s; 6.98, 1H, dd, J_o = 7.3 Hz and J_m = 2.0 Hz; 7.13, 1H, dd, J_o = 7.3 and J_o = 6.8 and 7.19, 1H, dd, J_o = 6.8 and J_m = 2.0). The splitting pattern of the four aromatic proton signals of this dimethoxydihydroxy fluorenone derivative clearly indicates that one of its benzene rings contains three adjacent aromatic protons while the other ring should be pentasubstituted showing the remaining aromatic proton as a singlet. On acetylation of the free phenolic OH group of dengibsinin, no significant deshielding of any aromatic proton was observed while on acetylation of the chelated phenolic OH, only one aromatic proton (dd, J = 7.3 and 2.0 Hz) suffers appreciable downfield shift by 0.6 ppm. Thus, there is no proton as the immediate neighbour of the free phenolic OH. The chelated phenolic OH has one *ortho* proton permitting its location at C-1. The disposition of the two OMe groups and the free phenolic OH group in the other ring was established as follows.

The chemical shift of the only aromatic singlet proton in **2**, **9** or **11** [δ 7.10 in **2**, 7.14 in **9** and 7.13 in **11** (Table 3)] indicates that the proton is not flanked by two OMe groups. The reported[3] chemical shift of H-4 of **8** is δ 6.75; substitution of its H-2 by OH or OMe would not be expected to deshield H-4 by ~ 0.35 ppm—the singlet is, therefore, due to the proton present at the *peri* positon of the carbonyl (C-8 in dengibsinin and its derivatives). As the free phenolic OH has no

Table 1. UV and visible spectral data of dengibsin (**1**), dengibsinin (**2**), their derivatives and fluorenone

Compd.	λ_{max}^{EtOH} nm (log ε)	$\lambda_{max}^{EtOH+NaOH}$ nm (log ε)
(**1**)	267(5.36), 275(5.40), 338(4.34) & 479.5 (4.08)	291.5(5.45) & 549.5(4.08)
(**4**)	265(4.56), 274(4.60) & 470(3.24)	252(4.36), 271(4.27), 293(4.15), 390 (3.32) & 552 (3.27)
(**5**)	274(4.58), 339(3.53) & 470(3.20)	—
(**6**)	243(4.29), 260(4.44), 271(4.42), 334(3.64) & 446.5(3.31)	—
(**7**)	258(4.46), 267(4.47) & 426(2.96)	—
(**2**)	264(4.37), 283(4.38), 309(4.03), 365(3.90) & 449.5(3.04)	261(4.24), 311(4.41), 406(4.08) & 505.5(3.71)
(**9**)	267(4.48), 274(4.45), 353(3.62) & 455(2.93)	263(4.56), 299(3.89), 360(3.49) & 543.5(3.10)
(**10**)	283(4.53), 366(3.92) & 450(2.93)	262(4.31), 312(4.42), 407(3.93) & 513(3.63)
(**11**)	277(3.56), 360(3.66) & 454(3.01)	—
(**12**)	258(4.50), 272(4.49), 352(3.46) & 453(3.13)	—
(**13**)	268(4.56), 310(3.30) & 415(2.79)	—
(**14**)	270(4.54), 310(3.34) & 423(2.86)	—
(**15**)	266(4.43), 274(4.47), 352(3.41) & 452.5(2.87)	—
Fluorenone	249(4.73), 257(4.86), 296 (3.47) & 380(2.39)	No change

Table 2. ^{1}H-NMR spectral data of dengibsin (1) and its derivatives (4–7)[a]

Compd.	Chemical shifts (δ), multiplicities and coupling constants (Hz)							
	C_1-OH/OCH_3[b]/ $OCOCH_3$	H-2	H-3	H-4	C_5-OH/OCH_3[b]/ $OCOCH_3$	H-6	C_7-OCH_3[b]	H-8
(1)	8.92, s	6.90–7.20, m			—	6.77, d (1.7)	4.08, s	6.82, d (1.7)
(4)	8.87, s	6.90–7.30, m			3.86, s	6.63, d (2.1)	4.03, s	6.95, d (2.1)
(5)	3.90, s	6.95–7.32, m			3.85, s	6.60, d (2.1)	3.90, s	6.91, d (2.1)
(6)	8.92, s	6.92–7.37, m			2.32, s	7.13, d (1.7)	4.05, s	6.85, d (1.7)
(7)	2.36, s	7.57, dd (7.5, 1.5)	6.98–7.40, m		2.31, s	7.12, d (1.8)	3.91, s	6.83, d (1.8)

[a] For 1, 100 MHz, d_6-acetone and for 4–7, 80 MHz, $CDCl_3$.
[b] The assignment of the OCH_3 signals of 4 and 5 may be interchanged.

ortho proton, one OMe group is allocated to C-7. Further, compound 15 (6-acetate-1-methyl ether), a derivative of 2 showed benzene-induced shift for two OMe-groups ($\Delta\delta$ = 0.6, 0.7 ppm, *vide* Table 3) having *ortho* protons.[4] So dengibsinin should possess structure 2 or 3. Structure 2 (≡ 1,6 - dihydroxy - 5,7 - dimethoxy - 9 - fluorenone) for dengibsinin has been finally settled on the basis of the following evidence.

(i) The aromatic singlet of 10 (in which the chelated OH is methylated) underwent downfield shift ($\Delta\delta$ = 0.08 ppm) by *in situ* reaction with trichloroacetyl isocyanate,[5] demonstrating the *meta* disposition of the proton with respect to the free phenolic OH group as in 2 (reported $\Delta\delta$ for H_{ortho} = 0.3–0.5, H_{meta} = 0.15 and H_{para} = 0.4 ppm).[5]

(ii) Upon NaOD–D_2O treatment of d_6-DMSO solution of 10 the aromatic singlet proton at δ 7.11 remained completely unexchanged even after a few days supporting its *meta* orientation with respect to the phenolic OH.

With a view to providing evidence for the presence of the 9-fluorenone moiety in both 1 and 2 a few reducing agents like Zn–Hg/HCl, Zn dust/NaOH and $NaBH_4$ were employed to effect the reduction of the carbonyl function of 2 while 9-fluorenone was used as the model compound. In the former two cases although CO reduction took place, the expected fluorene or the 9-fluorenol derivatives were not obtained. This behaviour may be ascribed to the presence of a number of oxygen substituents in the molecule.

Table 3. ^{1}H-NMR spectral data of dengibsinin (2) and its derivatives (9–15)[a,b]

Compd.	Chemical shifts (δ), multiplicities and coupling constants (Hz)							
	C_1-OH/OCH_3[c]/ $OCOCH_3$	H-2	H-3	H-4	C_5-OCH_3[c]	C_6-OH/OCH_3[c]/ $OCOCH_3$	C_7-OCH_3[c]	H-8
(2)	9.14, s	6.98, dd (7.3, 2)	7.13, dd (7.3, 6.8)	7.19, dd (6.8, 2)	4.14, s	6.12, s	3.96, s	7.10, s
(9)	9.10, s	6.99, dd (7.8, 1.5)	7.13, dd (7.8, 7.3)	7.20, dd (7.3, 1.5)	4.11, s	3.92, s	3.96, s	7.14, s
(10)	3.98, s	7.07, dd (8, 1.5)	7.22, t (8)	7.29, dd (8, 1.5)	3.96, s	6.12, s	3.90, s	7.13, s
(10) + TAI (6 hr)[5]	3.97, s	7.11, dd (8.3, 1.1)	7.27, dd (8.3, 7)	7.34, dd (7, 1.1)	3.93, s	—	3.87, s	7.21, s
(11)	3.98, s	7.07, dd (7.8, 1.5)	7.21, dd (7.8, 7.3)	7.29, dd (7.3, 1.5)	3.96, s	3.90, s	3.92, s	7.13, s
(12)	8.83, s	6.96–7.30, m			4.05, s	2.38, s	3.89, s	7.22, s
(13)	2.38, s	7.57, dd (8.3, 1)	7.27, dd (8.3, 6.8)	7.12, dd (6.8, 1)	3.89, s	2.36, s	3.81, s	7.19, s
(14)	2.34, s	7.55, dd (6.6, 1.5)	7.26, dd (7.2, 6.6)	7.09, dd (7.2, 1.5)	3.93, s	3.86, s	3.90, s	7.14, s
(15)	3.96, s	7.08, dd (8.5, 1.5)	7.24, dd (8.5, 7)	7.32, dd (7, 1.5)	3.88, s	2.37, s	3.82, s	7.17, s
(15) in C_6D_6[c]	3.28, s	6.52, dd (8.1, 1)	6.80, dd (8, 7.1)	7.42, dd (7.1, 1)	3.65, s	1.95, s	3.12, s	7.07, s

[a] Solvent $CDCl_3$ unless otherwise stated.
[b] Spectra of 2, 9, 11 and 13 at 200 MHz, 12 and 14 at 80 MHz and 10 and 15 at 270 MHz.
[c] The assignment of these OCH_3 signals may be interchanged.

However, conclusive evidence has been obtained from the $NaBH_4$ reduction. Thus the $NaBH_4$ reduction of **2** gave the corresponding alcohol, 1,6,9-trihydroxy-5,7-dimethoxyfluorene (**17**) [structure **2** having CHOH in place of CO] (yield ~ 80%), m.p. 180°, the ^{1}H-NMR signals for the carbinol moiety of which appeared at positions [δ 5.43 (1H, d, J = 8.4 Hz, collapsing to a singlet on D_2O shaking, —CHOH) and 1.88 (1H, d, J = 8.4 Hz, exchangeable with D_2O, —CHOH)] comparable to those of 9-fluorenol [δ 5.53 (1H, d, J = 8.5 Hz, collapsing to a singlet on D_2O shake) and 2.02 (1H, d, J = 8.5 Hz, exchangeable with D_2O], prepared in a similar manner from 9-fluorenone.

Baeyer–Villiger oxidation of **13** was also attempted. With *p*-nitroperbenzoic acid ($CHCl_3$, room temperature, 30 days) it remained completely unchanged. However, when the reaction was carried out in presence of *p*-toluenesulphonic acid under the same condition, it underwent deacetylation giving **12** (~ 15%) along with the other monoacetate **18** [structure **14** having 6-OH in place of 6-OCH_3] (~ 20%) and **2** (~ 50%).

Detailed studies on the reduction of fluorenone and its derivatives as well as the syntheses of the natural fluorenones (**1** and **2**) are in progress.

The formation of fluorenone derivative in the plant cells might have taken place from 9,10-phenanthraquinone *via* its enzymatic benzil–benzilic acid type rearrangement followed by enzyme catalysed elimination of elements of CO_2 and H_2 through a 6-membered cyclic transition state. Although phenanthrene and phenanthraquinone derivatives are known to occur in Orchidaceae, in absence of any experimental support this suggestion is just a speculative one which needs verification by biosynthetic experiments.

The other isolates of *D. gibsonii* were characterised by direct comparison (m.p., m.m.p., co-TLC and superimposable IR spectra) with authentic samples.[6,7]

EXPERIMENTAL

All m.ps were determined in open capillaries and are uncorrected. The UV spectra were taken in EtOH on a Varian Techtron Series 634 spectrophotometer and IR spectra as KBr pellets on a Pye Unicam SP 1025 spectrophotometer. The ^{1}H-NMR spectra were recorded on Varian CFT-20 (80 MHz), JEOL FX-100 (100 MHz), JEOL FX-200 (200 MHz) and Bruker (270 MHz) spectrometers, mass spectra at 70 eV and optical rotations on a Perkin–Elmer 241 polarimeter. The petrol refers to the 60–80° fraction and the silica gel used for column chromatography was of 100–200 mesh, unless otherwise stated. The TLC experiments were done on silica gel G.

Extraction: Air dried and powdered whole plant of *D. gibsonii* (3 kg) was extracted in a Soxhlet apparatus with petrol and $CHCl_3$ successively for 40 hr each. The marc left was then extracted with EtOH at room temp. The concentrates of the extracts were separately chromatographed over silica gel (60–100 mesh) using solvents and solvent mixtures of increasing polarities as eluents.

Compounds from the petrol extract

β-Sitosterol. The petrol–EtOAc (9:1) eluates afforded β-sitosterol (yield: 0.008%) m.p. and m.m.p. with an authentic sample 137°, $[\alpha]_D^{30} - 37°$ ($CHCl_3$).

Aurantiamide acetate (**16**). The concentrate of the earlier petrol–EtOAc (3:1) eluates on rechromatography over silica gel furnished **16** (0.0008%), crystallising from $CHCl_3$–petrol in fine colourless needles, m.p. and m.m.p. with an authentic sample[6] 184°, $[\alpha]_D^{30} - 65.8°$ ($CHCl_3$).

Dengibsinin (**2**). The concentrate of the later petrol–EtOAc (3:1) eluates on repeated chromatography over silica gel afforded **2** (0.003%), crystallising from $CHCl_3$–petrol in fine orange–red needles, m.p. 220°, IR: ν_{max}^{KBr} cm^{-1}: 3290, 1715, 1630, 1472, 1445, 1400, 1332, 1292, 1238, 1150, 1080, 923 and 765; MS *m/z* (rel. int.): 272 (100), 257 (46.9), 239 (6.4), 227 (5.4), 214 (9.4), 211 (15.6), 199 (5.4), 158 (5.2) and 136 (9.7).

Compounds from the $CHCl_3$ *extract*

Dengibsin (**1**). The concentrate of the petrol–EtOAc (7:3) eluates on rechromatography over silica gel furnished **1** (0.001%), crystallising from acetone–petrol in deep red needles, m.p. 227°, IR: ν_{max}^{KBr} cm^{-1}: 3330, 1715, 1630, 1335, 1280, 1160, 1040 and 975; MS *m/z* (rel. int.): 242 (100), 227 (81.2), 213 (15.4), 211 (10.6), 199 (73.1), 171 (42.7), 155 (22.3), 142 (20.8), 126 (25.1), 121 (30.4) and 115 (45.2). In addition to **1** the $CHCl_3$ extract afforded further amount of **2** (0.0018%).

Compound from the EtOH *extract*

Dimethyl terephthalate. The residue obtained from the petrol–EtOAc (9:1) eluates on rechromatography over silica gel afforded dimethyl terephthalate (0.0005%), crystallising from ether in colourless needles, m.p. and m.m.p. with an authentic sample[7] 140°.

Dengibsin monomethyl ether (**4**). To a soln of dengibsin (4 mg) in MeOH–Et_2O (1:2) a soln of CH_2N_2 in Et_2O was added. The mixture was kept overnight at room temp, the solvent was removed and the residue was crystallised from $CHCl_3$–petrol to afford **4** in red needles (3 mg), m.p. 152°, IR: ν_{max}^{KBr} cm^{-1}: 3320, 1715, 1620, 1500, 1320, 1275 and 1150.

Dengibsin dimethyl ether (**5**). Dengibsin (8 mg) was refluxed in Me_2CO with Me_2SO_4 (0.1 ml) in presence of dry K_2CO_3 (0.3 g) for 8 hr. The red solid obtained on working up the product in the usual way was chromatographed over silica gel. Petrol–EtOAc (85:15) eluates afforded **5**, crystallising from $CHCl_3$–petrol in red needles (5 mg), m.p. 122°, IR: ν_{max}^{KBr} cm^{-1}: 1715, 1610, 1320, 1280 and 1150.

Dengibsin monoacetate (**6**). To a soln of dengibsin (10 mg) in pyridine (0.5 ml) 2 drops of a soln of Ac_2O in pyridine (prepared by adding 2 drops of Ac_2O to 1 ml of pyridine) was added at 0° and the mixture was kept in the deep freeze for 10 hr. Usual work up of the mixture followed by chromatography of the product over silica gel afforded **6**, crystallising from $CHCl_3$–petrol in orange needles (6 mg), m.p. 159°, IR: ν_{max}^{KBr} cm^{-1}: 3350, 1780, 1715, 1620, 1370, 1310, 1265, 1210 and 1130.

Dengibsin diacetate (**7**). Dengibsin (5 mg) was acetylated (Ac_2O–Py, 24 hr) at room temp and the product was crystallised from $CHCl_3$–petrol. Dengibsin diacetate (**7**) was obtained in yellow needles (4 mg), m.p. 193°, IR: ν_{max}^{KBr} cm^{-1}: 1765, 1750, 1718, 1605, 1475, 1370, 1350, 1235, 1215 and 1200.

Dengibsinin 6-methyl ether (**9**). Dengibsinin (10 mg) was methylated with CH_2N_2 [*vide* preparation of **4**] and the product was crystallised from $CHCl_3$–petrol to afford **9** in red needles (9 mg), m.p. 163°, IR: ν_{max}^{KBr} cm^{-1}: 3310, 1740, 1628, 1497, 1395, 1327, 1278, 1235, 1142, 1092, 1010 and 768; M^+ 286.

Dengibsinin 1,6-dimethyl ether (**11**). To a soln of dengibsinin (10 mg) in MeOH (20 ml), Me_2SO_4 (1.0 ml) and NaOH soln (20%, 40 ml) were added and the mixture was refluxed for 6 hr. It was then diluted with H_2O and extracted with Et_2O. The concentrate of the ether extract was crystallised from $CHCl_3$–petrol to afford **11** in red needles (5 mg), m.p. 110°, IR: ν_{max}^{KBr} cm^{-1}: 3000, 1730, 1630, 1595, 1418, 1392, 1328, 1287, 1145, 1092, 1005 and 770; M^+ 300.

Dengibsinin 6-acetate (**12**). Dengibsinin (10 mg) was acetylated under mild conditon (*vide* preparation of **6**) and the product was purified by chromatography and then crystallised from $CHCl_3$–petrol to afford **12** in orange needles, (6 mg), m.p. 163°, IR: ν_{max}^{KBr} cm^{-1}: 3340, 1795, 1725, 1625, 1490, 1428, 1390, 1318, 1275, 1190, 1135, 1075, 1005, 923 and 763.

Dengibsinin 1,6-diacetate (**13**). Acetylation (Ac_2O–Py, 24 hr, room temp) of dengibsinin (6 mg) followed by crystallisation of the product from $CHCl_3$–petrol afforded **13** in yellow needles (4.5 mg), m.p. 180°, IR: ν_{max}^{KBr} cm^{-1}: 1780, 1740, 1640, 1380, 1322, 1235 and 1145; M^+ 356.

Dengibsinin 1-acetate-6-methyl ether (**14**). Acetylation (Ac_2O/Py, 24 hr, room temp) of **9** (5 mg) followed by crystallisation of the product from $CHCl_3$–petrol afforded **14** in yellow needles (3.5 mg), m.p. 130°, IR: ν_{max}^{KBr} cm^{-1}: 3080–2890, 1795, 1445, 1622, 1492, 1442, 1430, 1393, 1335, 1212, 1158, 1105, 1095, 1013 and 777.

Dengibsinin 6-acetate-1-methyl ether (**15**). Dengibsinin 6-acetate **11** (10 mg) was methylated with Me_2SO_4 (1.0 ml) in Me_2CO by refluxing in presence of dry K_2CO_3 (0.3 g) for 6 hr. Usual work up afforded an orange–red solid which was purified by chromatography over silica gel and then crystallised from $CHCl_3$–petrol to afford **15** in orange–red needles (9 mg), m.p. 140°, IR: ν_{max}^{KBr} cm^{-1}: 1775, 1715, 1610, 1480, 1380, 1315, 1270, 1200 and 1135.

Dengibsinin 1-methyl ether (**10**). Compound **15** (7 mg) was deacetylated with 5% ethanolic NaOH (24 hr, room temp). The product was chromatographed over silica gel and then crystallised from $CHCl_3$–petrol in orange needles (5 mg), m.p. 205°, IR: ν_{max}^{KBr} cm^{-1}: 3280, 1695, 1600, 1490, 1480, 1420, 1385, 1310, 1280, 1140 and 1050.

Sodium borohydride reduction of dengibsinin (**2**). To a soln of dengibsinin (5 mg) in dry MeOH (10 ml) $NaBH_4$ (100 mg) was added and the mixture was kept at room temp for 24 hr. The residue obtained on usual workup exhibited TLC spots for **2** and a more polar compound. Chromatography of this mixture over silica gel afforded dengibsinin (0.5 mg) and **17** (4 mg) from petrol–EtOAc (9:1) and petrol–EtOAc (4:1) eluates respectively. Compound **17** crystallised from EtOAc–petrol in colourless needles, m.p. 180°, IR: ν_{max}^{KBr} cm^{-1}: 3180–3380 (OH), 1618, 1583, 1480, 1458, 1370, 1313, 1230, 1145, 1085, 980, 760 and 720; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.88 (1H, d, J = 8.4 Hz, exchangeable with D_2O, CHO<u>H</u>), 3.98 and 4.12 (each 3H, s, C_5-OCH_3 and C_7-OCH_3), 5.43 (1H, d, J = 8.4 Hz, collapsing to a singlet on D_2O shake, C<u>H</u>OH), 5.71 (1H, s, exchangeable with D_2O, C_6-OH), 6.90 (1H, dd, J = 7.8 and 1.5 Hz, H-2), 7.04 (1H, s, H-8), 7.14 (1H, t, J = 7.8 Hz, H-3), 7.18 (dd, J = 7.6 and 1.5 Hz, H-4) and 9.41 (1H, s, exchangeable with D_2O, C_1-OH chelated with C_9-oxygen).

Attempted Baeyer–Villiger oxidation of dengibsinin 1,6-diacetate (**13**)

Formation of dengibsinin 1-acetate (**18**). To a soln of **13** (10 mg) in $CHCl_3$ (20 ml) *p*-nitroperbenzoic acid (8 mg, 1.56 mol equiv) and *p*-toluenesulphonic acid (2 mg) were added and the mixture was kept at room temp for 30 days. The $CHCl_3$ soln was then washed with 5% $NaHCO_3$ aq, dried over Na_2SO_4 and concentrated. The resulting residue was chromatographed over silica gel. The early petrol–EtOAc (4:1) eluates afforded **12** (1.3 mg) and the later ones **18** (1.7 mg). The petrol–EtOAc (3:1) eluates furnished **2** (3.8 mg). Compound **18** crystallised from $CHCl_3$–petrol in yellow needles, m.p. 193°, M^+ 314, ^{1}H-NMR (80 MHz, $CDCl_3$): δ 2.39 (3H, s, C_1-OCOC<u>H</u>$_3$), 3.90 and 3.97 (each 3H, s, C_5-OCH_3 and C_7-OCH_3), 6.07 (1H, br s, exchangeable with D_2O, C_6-OH), 7.14 (1H, s, H-8), 7.10–7.37 (2H, m, H-3 and H-4) and 7.54 (1H, dd, J = 8 and 1.5 Hz, H-2).

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REFERENCES

[1] B. Talapatra, P. Mukhopadhyay, P. Chaudhury and S. K. Talapatra, *Indian J. Chem.* **21B**, 386 (1982).
[2] J. D. Hooker, *The Flora of British India*, Vol. V, p. 746. L. Reeve, London (1890).
[3] J. Nakano, N. Katagiri and T. Kato, *Chem. Pharm. Bull.* **30**, 2590 (1982).
[4] R. G. Wilson, J. W. Bowie and D. H. Williams, *Tetrahedron* **24**, 1407 (1968).
[5] Z. Samek and M. Budéšinsky, *Coll. Czech. Chem. Commun.* **44**, 558 (1979).
[6] S. K. Talapatra, A. K. Mallik and B. Talapatra, *Phytochem.* **19**, 1199 (1980).
[7] B. Talapatra, G. Ray and S. K. Talapatra, *J. Indian Chem. Soc.* **60**, 96 (1983).