s, 3 × OMe). Found identical with the permethyl ether of natural **1b**. **1g**: colourless needles from MeOH, mp 180–182°; MS $[M]^+$ m/z 344 ($C_{19}H_{20}O_6$); ^1H NMR ($CDCl_3$, 60 MHz) 10.8 (1H, *br s*, exchangeable on addition of D_2O, –COOH), 6.0–7.5 (7H, *m*, ArH and –CH=), 4.10 (6H, *s*, 2 × OMe), 4.15 (6H, *s*, 2 × –OMe).

Diphenylmethylenedioxy derivative of **1b**. **1b** (50 mg) and diphenyldichloromethane (0.05 ml) were heated at 185° for 5 min. The reaction mixture was cooled, dissolved in C_6H_6 and passed through a small column of silica gel to give a solid (30 mg), crystallised from EtOH, mp 140–141°, MS $[M]^+$ m/z 410 ($C_{27}H_{22}O_4$).

Acknowledgements—The authors are grateful to Dr. Peerzada S. H. Khan, NBRI, Lucknow for his help in collection and identification of the plant material, to the instrumentation centre of IISC, Bangalore for some 270 MHz ^1H NMR spectra and CSIR, CCRUM and UGC, New Delhi for financial assistance.

REFERENCES

1. Prakash, S., Ahmad, J. and Zaman, A. (1981) *Phytochemistry* **20**, 1455.
2. Prakash, S., Wizarat, K., Zaman, A., Joshi, B. S., Gawad, D. H. and Likhate, M. A. (1983) *Indian J. Chem.* **22B**, 101.
3. Pfeiffer, P. and Sergiewskoja, S. (1911) *Chem. Ber.* **44**, 1107.
4. Minhaj, N., Khan, H., Kapoor, S. K. and Zaman, A. (1976) *Tetrahedron* **32**, 749.
5. Letcher, M. R., Nhamo, L. R. M. and Gumiro, I. T. (1972) *J. Chem. Soc. Perkin Trans.* 1 206.
6. Musgrave, O. C. (1957) *J. Chem. Soc.* 1104.

Phytochemistry, Vol. 24, No. 3, pp. 624–626, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00

THREE 3-BENZYL-4-CHROMANONES FROM *MUSCARI COMOSUM*

MATTEO ADINOLFI, GASPARE BARONE, ROSA LANZETTA, GUGLIELMO LAONIGRO, LORENZO MANGONI and MICHELANGELO PARRILLI*

Dipartimento di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, 80134 Napoli, Italy

(*Received* 26 *June* 1984)

Key Word Index—*Muscari comosum*; Liliaceae; bulbs; 3-benzyl-4-chromanones; homoisoflavanones; 5,8-dihydroxy-3-(4′-hydroxybenzyl)-6,7-dimethoxy-4-chromanone; 5,7-dihydroxy-3-(3′-hydroxy-4′-methoxybenzyl)-4-chromanone; 5,7-dihydroxy-3-(4′-hydroxybenzyl)-4-chromanone.

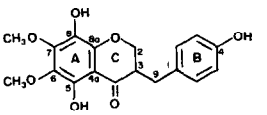
Abstract—Three novel 3-benzyl-4-chromanones have been isolated from the bulbs of *Muscari comosum*.

INTRODUCTION

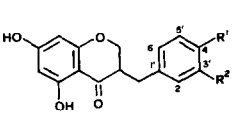
We recently [1] described the structural elucidation of three components of the homoisoflavanone fraction extracted from the bulbs of *Muscari comosum*. In the present paper we report the spectral data which now allow us to assign structures **1**, **2** and **3** to a further three homoisoflavanones from the same source, named muscomin, 3′-hydroxy-3,9-dihydroeucomin and 4′-demethyl-3,9-dihydroeucomin, respectively. It is noteworthy that **1** and **2**, as compared to known 3-benzyl-4-chromanones [2], possess new oxygenation patterns. Compound **1** bears oxygen functions at both positions 6 and 8 of ring A in addition to the normally oxygenated functions 5 and 7, and compound **2** bears a hydroxyl group at the 3′ position like scillascillins, although it does not possess the 3-spirocyclobutene ring which is characteristic of these compounds.

RESULTS AND DISCUSSION

Compound **1** possesses the molecular formula $C_{18}H_{18}O_7$ (high-resolution mass spectrum). In the ^1H NMR spectrum the signals of the protons of rings B and C were clearly seen (Table 1). The remaining resonances were those of three hydroxyl and two methoxyl groups. The appearance of the hydroxytropylium fragment (m/z 107) in the mass spectrum indicated that one hydroxyl group was at the 4′ position. It was assigned the δ9.31 ^1H NMR signal because an NOE was measured between this and the 3′,5′ signals. The UV absorption at



1



2 R¹ = OCH₃ R² = OH
3 R¹ = OH R² = H

*To whom correspondence should be addressed.

Table 1. ^{1}H NMR (270 MHz) chemical shifts in DMSO-d_6*

Compound	C-2	C-3	C-5	C-7	C-6, C-8	C-9	C-2', C-6'	C-3', C-5'	C-4'
1	4.16 *m* 4.34 *m* AB of ABX	3.06 *m*	11.58 †*s*	3.94 *s*	3.76 *s*/8.59 †*s*	2.67 *d* 3.06 *m*	7.09 *d*	6.75 *d* *J* = 7.93 AA'BB'	9.31 †*s*
2	4.08 *m* 4.26 *m* AB of ABX	2.98 *m*	12.18 †*s*	10.84 †*s*	5.87/5.88 *J* = 3.7 AB	2.56 *m* 2.98 *m*	6.66 *d* (C-2') *J* = 1.8 6.61 *dd* (C-6') *J* = 1.8 *J* = 7.93	6.84 *d* (C-5') *J* = 7.93 8.95 *br s* (C-3')	3 74 *s*
3	4.10 *m* 4.28 *m* AB of ABX	2.97 *m*	12.24 †*s*	10.60 †*s*	5.87 *brs*	2.63 *m* 3.05 *m*	7.07 *d*	6.74 *d* *J* = 7.93 AA'BB'	9.35 †*b*

*All chemical shifts are given in δ (ppm). Coupling constants are given in Hz.
†Protons exchangeable with D_2O.

288 nm was shifted (35 nm) upon addition of aluminium chloride. This indicated [3] the presence of a hydroxyl group at C-5 (δ11.58, chelated). When the δ11.58 signal was irradiated, the methoxyl signal at δ3.76 appeared enhanced. Therefore the C-6 bears a methoxyl group. The second methoxyl group is at C-7 as the UV absorption remained unaffected upon addition of sodium acetate [3]. Accordingly, the signal of the hydroxyl group at C-8 appearing at δ8.59 was enhanced upon irradiation of the 7-methoxyl signal at δ3.94. The ^{13}C NMR spectrum of muscomin (Table 2) was in accordance with structure **1**.

Compound **2** possesses the molecular formula $C_{17}H_{16}O_6$ (high-resolution mass spectrum). In the mass spectrum of homoisoflavanones the base peak is usually the ring-B tropylium ion [2]; the *m/z* value, 137, of this peak in the case of **2** indicated that ring B bears one hydroxyl and one methoxyl group. In the ^{1}H NMR spectrum the signals of the protons at C-2' (δ6.66, *d*, J_{meta} = 1.8 Hz), C-5' (δ6.84, *d*, J_{ortho} = 7.93 Hz) and C-6' (δ6.61, *dd*, J_{meta} = 1.8 Hz and J_{ortho} = 7.93 Hz) are clearly discerned. The ring-B hydroxyl (δ8.95 *br s*) and methoxyl (δ3.74 *s*) groups are linked at positions 3' and 4', respectively, since irradiation of the signal at δ3.74 caused an NOE enhancement of the 5'-H signal. Two hydroxyl protons appear at δ12.18 *s* (5-OH, chelated) and δ10.84 *s* (7-OH). Irradiation of the latter signal caused enhancement of the signal of the protons at C-6 and at C-8. The UV absorption at 287 nm of **2** was shifted upon both addition of sodium acetate (36 nm; indicating the presence of a free hydroxyl at C-7) and aluminium chloride (34 nm; indicating the presence of a free hydroxyl at C-5). The ^{13}C NMR data of **2** are summarized in Table 2.

Table 2. ^{13}C NMR (67.88 MHz) chemical shifts of **1**, **2** and **3** in DMSO-d_6*

Carbon	1	2	3
2	69 0	68.9	68.8
3	46.3	45.4	45.5
4	199.7	197.7	197.7
4a	103.3	101.2	101.0
5	147.3†	163.8	163.6
6	133.5‡	95.9	95.9
7	150.1†	166.6	166.7
8	130.1‡	94.7	94.7
8a	145.2†	162.8	162.6
9	30.9	31.2	31.2
1'	128.0‡	130.6	128.0
2'	129.9	119.5‡	129.8
3'	115.2	146.3†	115.1
4'	155.5†	146.5†	155.5
5'	115.2	112.3‡	115.1
6'	129.9	116.2‡	129.8
OMe	60.7	55.6	
OMe	60.5		

*Chemical shifts are given in δ (ppm) relative to TMS. The assignments are based on on- and off-resonance spectra and on comparison with data from ref. [2].
†,‡Interchangeable values.

Compound **3** possesses the molecular formula $C_{16}H_{14}O_5$ (high-resolution mass spectrum). The hydroxytropylium peak (*m/z* 107) displayed by the mass spectrum and the AA'BB' signals at δ7.07 and 6.74 (J = 7.93 Hz) indicated the substitution pattern of ring B. The substitution pattern of ring A was deduced from the UV absorption (287 nm) bathochromic shifts caused by both the addition of sodium acetate and of aluminium chloride (35 and 34 nm, respectively). The ^{13}C NMR data (Table 2) and the remaining ^{1}H NMR signals (Table 1) fully agree with structure **3**, 4'-demethyl-3,9-dihydropunctatin, which is identical to the structure assigned to a homoisoflavanone isolated from *Eucomis bicolor* [4] and cited in Heller and Tamm's review [2] without a description of its physical or spectral properties.

EXPERIMENTAL

Isolation of 3-benzyl-4-chromanones **1**, **2** *and* **3**. Compounds **1**, **2** and **3** were obtained from fractions *e*, *d* and *c*, respectively, isolated from the bulbs of *M comosum* Mill. by the procedure described previously [1].

Compound **1** (100 mg) was the major component isolated by TLC [hexane–Et_2O–dioxane (5:3:2), 3 runs] from the mother

liquors of the crystallization ($CHCl_3$) of fraction *e*. It had mp 131–132° (from $CHCl_3$), $[\alpha]_D$ −71° (dioxane; *c* 0.6). UV λ_{max}^{MeOH} nm (log ε): 288 (4.25). EIMS, 70 eV, *m/z* (rel. int.): 346.1048 ($[M]^+$; calc. for $C_{18}H_{18}O_7$: 346.1052) (20), 107 (100).

Compound **2** (20 mg) was isolated by TLC [C_6H_6–EtOAc (23:2), 3 runs] of the crystals obtained by crystallization ($CHCl_3$) of fraction *b*. It had mp 136–138° (from $CHCl_3$), $[\alpha]_D$ −51° (MeOH; *c* 0.7). UV λ_{max}^{MeOH} nm (log ε): 287 (4.38). EIMS, 70 eV, *m/z* (rel. int.): 316.0952 ($[M]^+$; calc. for $C_{17}H_{16}O_6$: 316.0947) (25), 137 (100).

Compound **3** (20 mg) was obtained by TLC [C_6H_6–EtOAc (23:2), 3 runs] from the mother liquors of the crystallization ($CHCl_3$) of fraction *c*. It had mp 103–104° (from C_6H_6–MeOH), $[\alpha]_D$ −34° (MeOH; *c* 0.4) UV λ_{max}^{MeOH} nm (log ε): 287 (4.22). EIMS, eV, *m/z* (rel. int.): 286.0849 ($[M]^+$, calc. for $C_{16}H_{14}O_5$. 286.0841) (20), 107 (100).

Acknowledgements—This work was supported by the Ministero della pubblica Istruzione. NMR spectra were performed at the Centro di Metodologie Chimico-Fisiche della Università di Napoli.

REFERENCES

1. Adinolfi, M., Barone, G., Belardini, M., Lanzetta, R., Laonigro, G. and Parrilli, M. (1984) *Phytochemistry* **23**, 2091.
2. Heller, W. and Tamm, C. (1981) *Fortschr. Chem. Org. Naturst.* **40**, 105.
3. Markham, K. R. and Mabry, T. J. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.), p. 45. Chapman & Hall, London.
4. Schaad, W. (1977) Ph.D. Thesis, Basel.

Phytochemistry, Vol. 24, No. 3, pp. 626–628, 1985.
Printed in Great Britain.

0031-9422/85 $3.00 + 0.00

LIGNAN FROM CALYCES OF *DIOSPYROS KAKI*

SHIN MATSUURA and MUNEKAZU IINUMA*

Institute of Pharmacognosy, Gifu College of Pharmacy, 5-6-1 Mitahora-higashi, Gifu 502, Japan

(*Received* 20 *June* 1984)

Key Word Index—*Diospyros kaki*; Ebenaceae, calyx, (−)-divanillyltetrahydrofuran ferulate.

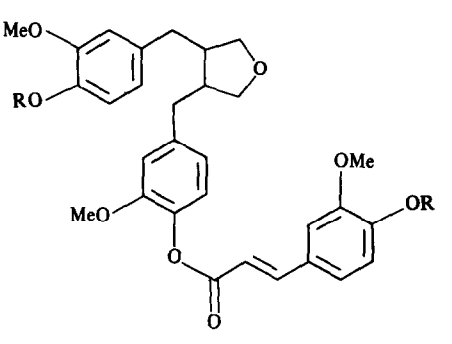
Abstract—From *Diospyros kaki* calyces, a new lignan was isolated. Its structure was elucidated as (−)-divanillyltetrahydrofuran ferulate by spectroscopic methods and was established by total synthesis.

INTRODUCTION

Calyces of *Diospyros kaki* are used both in Japanese folk medicine and in traditional Chinese medicine for the treatment of hiccough. In previous papers [1, 2], as the constituents of the calyces, 18 compounds comprising flavonols and their glycosides, triterpenoids and aromatic acids were isolated and their structures determined. The present paper deals with the structural elucidation of a new lignan and its confirmation by total synthesis.

RESULTS AND DISCUSSION

Compound **1** (R = H) was isolated from the crude acetone extract of the calyces of *D. kaki* by repeated column chromatography on silica gel, mp 184–185°, $[\alpha]_D$ −58.3° (THF), as colourless needles, and formed a diacetate ($[M]^+$ 622) and a di-*O*-methyl ether (**2**) (R = Me) ($[M]^+$ 548), respectively. The mass spectrum of **1** ($[M]^+$ 520) and elemental analysis indicated that it had the molecular formula $C_{30}H_{32}O_8$. In particular, the presence of ions at *m/z* 137 and 138 is characteristic of the vanillyl group. In the ^1H NMR spectrum, the two-proton signal at δ2.15 and the four-proton one at δ2.74 confirmed a tetrahydrofuran ring, which was further confirmed by the signals at δ63.7 (triplet) and 39.4 (doublet) in the



1 R = H
2 R = Me