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OXYGENATED PYRENES, THEIR POTENTIAL BIOSYNTHETIC PRECURSOR AND BENZYLATED DIHYDROFLAVONES FROM TWO AFRICAN *UVARIA* SPECIES*

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Key Word Index—*Uvaria doeringii*; *U. lucida* spp. *lucida*; Annonaceae; 2,7-dihydroxy-1,8-dimethoxypyrene; 2-hydroxy-1,7,8-trimethoxypyrene; 1,2-dihydro-2,9-dihydroxy-10-methoxy-furo[2,3-a]phenanthrene; chamanetin; isochamanetin; dichamanetin; uvarinol; isouvarinol.

Abstract—Two new oxygenated pyrenes, 2,7-dihydroxy-1,8-dimethoxypyrene and 2-hydroxy-1,7,8-trimethoxy-pyrene, have been isolated, from the stem bark of Tanzanian *Uvaria lucida* spp. *lucida*, along with the benzylated dihydroflavones chamanetin, isochamanetin, dichamanetin, uvarinol and isouvarinol, and the carotenoid lutein. 2,7-Dihydroxy-1,8-dimethoxypyrene was also isolated from Ghanaian *U. doeringii*, together with a potential biogenetic precursor of the pyrenes, 1,2-dihydro-2,9-dihydroxy-10-methoxy-furo[2,3-a]phenanthrene, and most of the benzylated flavanones, which were found in *U. lucida* spp. *lucida*. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

In recent years, plants of the genus *Uvaria* have been the focus of intensive phytochemical investigations, owing to the fact that these species are known to be rich sources of natural products with interesting chemical structures and bioactivities [2, 3]. We recently investigated several African *Uvaria* species [4, 5], some of which are used locally as remedies for malaria [6].

From Tanzanian *U. lucida* spp. *lucida* and West African *U. doeringii* we have now isolated and identified two oxygenated pyrenes and a potential biogenetic precursor of this class of fused aromatic polycyclic compounds.

Uvaria lucida spp. *lucida* is an erect shrub or liane that grows in lowland dry evergreen forests, wooded grasslands and bushlands of Kenya and Tanzania [7]. In Tanzania, decoctions from the stem and root barks are used as remedies for malaria and stomach disorders. Extracts from the root and stem barks have been found to inhibit the growth of the multidrug resistant K1 strain of *Plasmodium falciparum*, the malaria parasite, *in vitro* [6]. Chemical investigation of the root bark has yielded the dihydrochalcones uvaretin, diuvaretin and chamuvaritin, together with the hitherto unknown bis-(benzopyranyl) sesquiterpene, lucidene [8]; the dihydrochalcones are mildly active against *P. falciparum in vitro* [6]. It was of interest therefore to study also the constituents of the stem bark.

There do not appear to be any reported phytochemical data for *U. doeringii*. This species grows as a scrambling shrub in coastal thickets of Togo and Ghana; roots and leaves are used against various diseases [9].

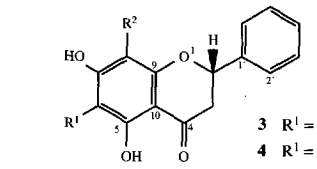
RESULTS AND DISCUSSION

Repeated chromatography of the $CHCl_3$ extract of the stem bark of *U. lucida* ssp. *lucida* yielded the pyrenes **1** and **2**, in addition to the known compounds chamanetin (**3**), isochamanetin (**4**), dichamanetin (**5**), uvarinol (**6**), isouvarinol (**7**) and lutein. Using similar methods for the separation of the methanol extract of the twigs of *U. doeringii* compounds **1** and **4–8** were isolated and lutein was found in the petrol extract; however, compounds **2** and **3** could not be detected.

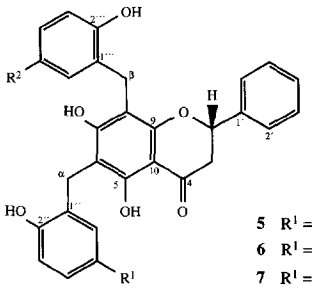
The known compounds **3–7** and lutein were identified by comparison of their physicochemical properties with literature data [10–15]. Since there are some discrepancies with the NMR data cited in the literature especially for those of **7** [13], the NMR spectra of the isolated flavanones **3–7** were examined in detail by HMQC and HMBC. This allowed the unequivocal

*Part 76 in the series 'Constituents of Tropical Medicinal Plants'. For Part 75 see ref. [1]. This paper is dedicated to Prof. Dr G. Seitz, Marburg, on the occasion of his 60th birthday.

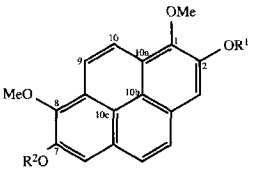
†Author to whom correspondence should be addressed.



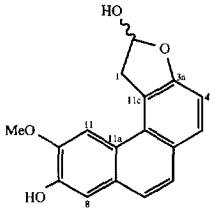
3 $R^1 = H$, $R^2 = 2'''$-Hydroxybenzyl
4 $R^1 = 2''$-Hydroxybenzyl; $R^2 = H$



5 $R^1 = R^2 = H$
6 $R^1 = 2''''$-Hydroxybenzyl; $R^2 = H$
7 $R^1 = H$, $R^2 = 2'''''$-Hydroxybenzyl



1 $R^1 = R^2 = H$
2 $R^1 = H$; $R^2 = Me$
9 $R^1 = R^2 = Me$



8

attachment of all ^1H and ^{13}C NMR signals (Tables 1 and 2).

Compound **1** gave a mass spectrum with a $[M]^+$ at *m/z* 294 (high-resolution mass spectrometry: $C_{18}H_{14}O_4$). The UV/VIS spectrum indicated a fused aromatic system. In the ^1H NMR spectrum (Table 3) only five singlets were observable with relative intensities of 3:1:1:1:1. Furthermore, the ^{13}C NMR spectrum (Table 4) showed only nine signals, thus suggesting the presence of a symmetrical molecule, the structure of which resulted from NOE measurements (Fig. 1).

Final proof of the structure was obtained from the methylation product of compound **1**, 1,2,7,8-tetramethoxypyrene (**9**), which was found to be identical with the methylation product of compound **2**.

Compound **2** showed spectral properties very similar to those of compound **1**. However, the $[M]^+$ was found to have 14 mu more than compound **1**. Furthermore, the ^1H and ^{13}C NMR spectra exhibited the full set of resonances which are consistent with the molecular formula (high-resolution mass spectrometry: $C_{19}H_{16}O_4$) and, in particular, three signals due to the methoxyl groups were detected. This revealed compound **2** to be a monomethyl derivative of compound **1**. The position of the 'additional' methyl group and the structure of compound **2** were finally established by heteronuclear correlation spectroscopy (Fig. 2) and NOE measurements (Fig. 3).

Compound **8**, like compounds **1** and **2**, showed all the features of a fused aromatic system. But, in addition, in the aliphatic region of the ^1H NMR spectrum the resonances of an ABX-system appeared, in addition to the singlet due to one methoxyl group (Table 5). The complete structure of compound **8** was deduced from heteronuclear correlation experiments (Fig. 4) and this was also confirmed by NOE measurements.

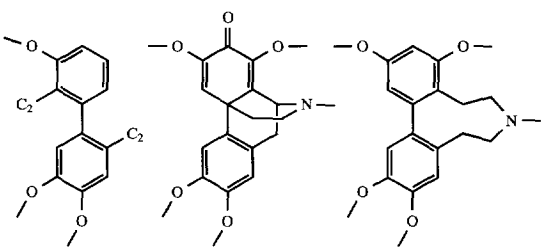
Nitrogen-free natural products with the carbon skeleton of phenanthrenes or partially hydrogenated phenanthrenes have occasionally been isolated from species of various families [16–18]; however, according to our knowledge, there are no reports of secondary plant metabolites with the carbon skeleton of pyrenes. Very recently the isolation of the tetrahydropyren-3-one ochrolone has been described from *Coelogyne ochracea* (Orchidaceae) [19]. Different biogenetic pathways for the formation of naturally occurring phenanthrenes have been discussed [17], which use either shikimic acid/phenylpropane or mevalonic acid as precursors. The latter pathway generates alkyl-substituted phenanthrenes, such as the micrandrols [17]. Another suggested route to 9,10-dihydrophenanthrenes starts from 1,2-diphenylethanes [20]. The biogenetic precursor of compound **8** might have a bis-phenylethane structure, like compound **10**. This hypothetical intermediate potentially could be derived from a 1-benzyltetrahydroisoquinoline alkaloid by phenol oxidation to compound **11** and subsequent rearrangement to a dibenzazonine-type structure **12** [20–22]. These considerations are supported by the fact that alkaloids of type **11** are known to occur in species of the Annonaceae [23]. Oxidative desamination and desoxygenation of compound **12** might bring about the formation of compound **10**.

We now consider the pyrenes **1** and **2** to originate from a phenanthrene such as compound **8**.

In the brine shrimp bioassay [24], pyrene **2** showed cytotoxicity comparable with that of podophyllotoxin and compound **8** exhibited about half the activity of podophyllotoxin. Surprisingly, pyrene **1** was distinctly less active. Cytotoxicity and antimicrobial activities have already been reported for the flavonoids **3–6**, [10, 12, 25].

EXPERIMENTAL

General. Mps uncorr. TLC was performed on ready-made plates (nano-plates® SIL-20 UV_{254}, Macherey–Nagel or Merck) using $CHCl_3$–MeOH (19:1), unless



10 **11** **12**

Table 1. ^{1}H NMR data for compounds **3–7** (δ, J [Hz] in CD_3COCD_3)

H	3	4	5	6	7
2	5.61 *dd* (12.5, 3)	5.58 *dd* (13, 3)	5.58 *dd* (12.5, 3)	5.60 *dd* (12.5, 3)	5.54 *dd* (13, 3)
3	2.86 *dd* (17, 3)	2.83 *dd* (17, 3)	2.84 *dd* (17, 3)	2.87 *dd* (17, 3)	2.82 *dd* (17, 3)
	3.17 *dd* (17, 12.5)	3.19 *dd* (17, 13)	3.15 *dd* (17, 12.5)	3.18 *dd* (17, 12.5)	3.17 *dd* (17, 13)
6	6.08 *s*	–	–	–	–
8	–	6.11 *s*	–	–	–
2′, 6′	7.56 *m*	7.57 *m*	7.58 *m*	7.57 *m*	7.57 *m*
3′, 5′	7.44 *m*	7.45 *m*	7.44 *m*	7.44 *m*	7.44 *m*
4′	7.38 *m*	7.39 *m*	7.38 *m*	7.38 *m*	7.38 *m*
α	–	3.89 *s*	3.89 *s**	3.89 *s*	3.90 *s*
3″	–	6.84 *dd* (8, 1)	6.83 *dd* (8, 1)	6.75 *d* (8)	6.84 *dd* (7.5, 1)
4″	–	7.01 *ddd* (8, 7.5, 2)	7.01 *ddd* (8, 7.5, 2)	6.90 *dd* (8, 2)	7.02 *ddd* (7.5, 7.5, 2)
5″	–	6.74 *ddd* (7.5, 7.5, 1)	6.73 *ddd* (7.5, 7.5, 1)	–	6.75 *ddd* (7.5, 7.5, 1)
6″	–	7.15 *dd* (7.5, 2)	7.26 *dd* (7.5, 2)	7.27 *d* (2)	7.19 *dd* (7.5, 2)
β	3.40 *s*	–	3.91 *s**	3.86 *d* (15)	3.85 *s*
				3.90 *d* (15)	
3‴	6.82 *dd* (8, 1)	–	6.81 *dd* (8, 1)	6.82 *dd* (7.5, 1)	6.73 *d* (8)
4‴	7.00 *ddd* (8, 7.5, 2)	–	6.99 *ddd* (8, 7.5, 2)	7.00*	6.89 *dd* (8, 2)
5‴	6.70 *ddd* (7.5, 7.5, 1)	–	6.68 *ddd* (7.5, 7.5, 1)	6.68 *ddd* (7.5, 7.5, 1)	–
6‴	7.04 *dd* (7.5, 2)	–	7.10 *dd* (7.5, 2)	7.05 *dd* (7.5, 2)	7.11 *d* (2)
α'	–	–	–	3.77 *s*	–
3⁗	–	–	–	6.82 *dd* (7.5, 1)	–
4⁗	–	–	–	7.00*	–
5⁗	–	–	–	6.71 *ddd* (7.5, 7.5, 1)	–
6⁗	–	–	–	6.98*	–
β'	–	–	–	–	3.75 *s*
3⁗′	–	–	–	–	6.79 *dd* (7.5, 1)
4⁗′	–	–	–	–	6.97 *ddd* (7.5, 7.5, 2)
5⁗′	–	–	–	–	6.66 *ddd* (7.5, 7.5, 1)
6⁗′	–	–	–	–	6.84 *dd* (7.5, 2)
5-OH	12.15 *s*	12.7 *s*	12.7 *s*	12.7 *s*	12.7 *s*
7-OH	9.2 *br s*	9.2 *br s*	9.0 *br s*	10.9 *s*	10.9 *s*
2″-OH	–	9.2 *br s*	9.0 *br s*	9.1 *br s*	9.1 *br s*
2‴-OH	9.2 *br s*	–	9.0 *br s*	9.1 *br s*	9.1 *br s*
24-OH	–	–	–	8.2 *br s*	–
2⁗-OH	–	–	–	–	8.2 *br s*

* Signals overlapped.

otherwise stated; detection by UV and anisaldehyde reagent [26]. For CC, silica gel 60 (Macherey–Nagel or Merck), Fractogel PVA 500 (Merck) or Sephadex® LH 20 (Pharmacia) were used. Unless otherwise stated, IR were run in KBr, $[\alpha]_D$ at 21° in Me_2CO, UV/VIS in MeOH. ^{1}H NMR were run at 360 MHz (int. standard: TMS), ^{13}C NMR at 90 MHz (int. standard: solvent). MS were recorded in EI mode (70 eV) using a direct inlet.

Plant material. Stem bark of *U. lucida* ssp. *lucida* Benth. was collected from Vigwaza Forest, Chalinze (Coast Region), Tanzania, in December 1994. The plant was authenticated by Mr L. B. Mwasumbi of the Herbarium, Department of Botany, University of Dar es Salaam, where a voucher specimen is preserved (Mwasumbi coll. No. 14230). *U. doeringii* Diels was collected from the western region of Ghana and identified by Mr A. A. Enti, Forestry Enterprises, Legon, Ghana, in June 1994. A herbarium specimen is kept under voucher No. 9402 in the Institute of Pharmacy and Food Chemistry, University of Erlangen.

Extraction and separation. Uvaria lucida ssp. *lucida.* Air-dried and pulverized stem bark (2 kg) was soaked in $CHCl_3$ at *ca* 30° for 3 days. The concd extract (50 g) was sepd by vacuum liquid chromatography (VLC) over silica gel with *n*-hexane containing increasing amounts of EtOAc into 16 frs. The less polar frs 1–7 consisted of complex mixtures and/or unstable compounds and thus were not analysed further. Sepn of the combined frs 8–16 by CC (silica gel, hexane–EtOAc mixts) and subsequent purification by CC on Sephadex® LH 20 (MeOH) yielded compounds **1–7** and lutein.

Uvaria doeringii. Dried and pulverized twigs (1.2 kg) were extracted first with petrol and then MeOH to yield 4.9 g of petrol extract and 63.5 g of MeOH extract. The MeOH extract was redissolved in a mixt. of 400 ml MeOH and 600 ml H_2O and the suspension obtained was successively extracted with petrol (3.5 g extract), CH_2Cl_2 (6.5 g extract) and EtOAc (6.8 g extract). The CH_2Cl_2 extract was sepd by MPLC (silica gel, $CHCl_3$–MeOH, 49:1) into seven frs. Repeated CC on silica gel (petrol–Me_2CO mixts) or on Sephadex® LH 20 (MeOH–$CHCl_3$, 9:1) and subsequent purification by CC on PVA 500 (MeOH–$CHCl_3$, 9:1) yielded compounds **1** and **4–8**. Lutein was isolated from the petrol extract together with some sterols.

2,7-*Dihydroxy*-1,8-*dimethoxypyrene* (**1**). Light yel-

Table 2. ^{13}C NMR data for compounds **3–7** (δ in CD_3COCD_3)

C	3	4	5	6	7
2	79.9	80.0	79.9	79.8	80.0
3	43.5	43.7	43.6	43.6	43.8
4	197.3	197.1	197.0	197.0	196.8
5	163.4	162.5	160.7	160.8	160.7
6	97.0	108.2	108.8	108.9	108.8
7	165.0	165.2	164.4	164.5	165.0
8	107.3	95.9	107.9	107.8	108.2
9	161.4	162.3	159.5	159.4	159.5
10	103.5	103.2	102.9	102.9	102.4
1′	140.1	140.2	140.4	140.4	140.4
2′, 6′	127.2	127.3	127.2	127.2	127.3
3′, 5′	129.5	129.5	129.5	129.5	129.5
4′	129.3	129.4	129.3	129.3	129.3
α	–	22.4	23.0	23.1	23.1
1″	–	127.6	128.0	127.6	128.1
2″	–	155.2	155.1	152.9	155.5
3″	–	116.0	116.1[a]	115.8[b]	116.1
4″	–	127.9	127.9	128.4	127.7
5″	–	120.6	120.7	133.5	120.2[a]
6″	–	130.9	131.4	132.3	131.2
β	23.0	–	23.7	23.7	23.8
1‴	127.6	–	128.0	128.0	127.7
2‴	155.2	–	155.1	155.3	153.0
3‴	115.8	–	116.0[a]	115.8[b]	115.7
4‴	127.8	–	127.9	127.8	128.4
5‴	120.6	–	120.7	120.3[a]	133.2
6‴	130.6	–	131.2	131.0	132.1
α'	–	–	–	35.4	–
1⁗	–	–	–	129.1	–
2⁗	–	–	–	155.7	–
3⁗	–	–	–	115.9[b]	–
4⁗	–	–	–	127.8	–
5⁗	–	–	–	120.5[a]	–
6⁗	–	–	–	131.2	–
β'	–	–	–	–	35.5
1⁗	–	–	–	–	129.5
2⁗	–	–	–	–	155.7
3⁗	–	–	–	–	115.7
4⁗	–	–	–	–	127.7
5⁗	–	–	–	–	120.4[a]
6⁗	–	–	–	–	131.0

[a,b] Assignments may be interchanged.

Table 3. ^1H NMR data for compounds **1**, **2** and **9** (δ, J [Hz] in CD_3COCD_3)

H	1	2	9
3	7.75 *s*	7.91 *s*	7.92 *s*
4	7.86 *s*	7.96 *d* (9)	7.99 *s*
5	7.86 *s*	7.89 *d* (9)	7.99 *s*
6	7.75 *s*	7.76 *s*	7.92 *s*
9	8.26 *s*	8.24 *d* (9.5)	8.27 *s*
10	8.26*s*	8.29 *d* (9.5)	8.27 *s*
2-OH	8.62 *s*	–	–
7-OH	8.62 *s*	8.68 *s*	–
1-OMe	4.09 *s*	4.09 *s*	4.09 *s*
2-OMe	–	4.13 *s*	4.14 *s*
7-OMe	–	–	4.14 *s*
8-OMe	4.09 *s*	4.08 *s*	4.09 *s*

Table 4. ^{13}C NMR shifts of compounds **1**, **2** and **9** (δ in $CDCl_3$)

C	1*	2*	9
1	141.5	142.9	143.5
2	146.8	149.7	150.4
3	112.4	108.7	108.8
3a	127.3	127.1	127.4
4	125.3	125.7	125.9
5	125.3	125.5	125.9
5a	127.3	127.7	127.4
6	112.4	112.4	108.8
7	146.8	147.1	150.4
8	141.5	141.7	143.5
8a	123.4	123.6	124.3
9	120.5	120.9	121.6
10	120.5	121.0	121.6
10a	123.4	123.7	124.3
10b	120.0	120.4	120.6
10c	120.0	120.0	120.6
1-OMe	61.2	61.6[a]	61.8
2-OMe	–	56.0	56.3
7-OMe	–	–	56.3
8-OMe	61.2	61.5[a]	61.8

* With addition of 15% CD_3OD.
[a] Assignments may be interchanged.

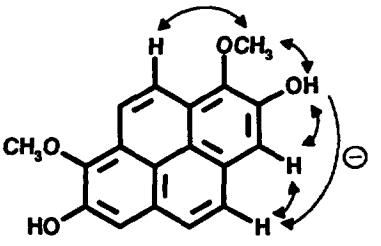


Fig. 1. NOEs observed for compound **1**.

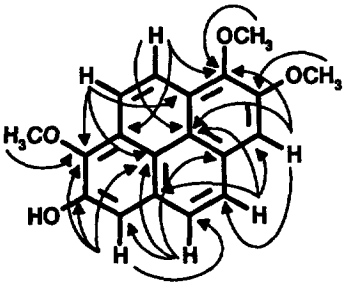


Fig. 2. Important long-range correlations observed in the HMBC of **2**.

low crystals from *t*-BuOMe (24 mg from *U. lucida*; 4 mg from *U. doeringii*), mp 255–256°. TLC: R_f 0.59; anisaldehyde: turquoise. IR ν_{max} cm^{-1}: 3306, 2936, 1589, 1511, 1459, 1429, 1401, 1271, 1208, 1177, 1021, 998. UV λ_{max} nm (log ε): 252 (4.83), 271 (sh, 4.31), 280 (4.28), 304 (3.58), 319 (3.95), 334 (4.27), 350 (4.43), 377 (3.46), 398 (3.64). ^1H NMR: Table 3. ^{13}C NMR: Table 4. MS *m/z* (rel. int.): 294.0895 $[M]^+$ (92) (calcd for $C_{18}H_{14}O_4$: 294.0892), 280 (18), 279.0662

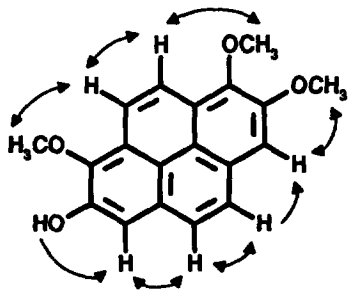


Fig. 3. NOEs observed for **2**.

Table 5. ^{1}H and ^{13}C NMR data for compound **8** (δ, J [Hz] in CD_3OD)

Position	C	H
1	42.5	3.71 *dd* (16, 2.5) 4.06 *dd* (16, 7)
2	101.8	6.19 *dd* (7, 2.5)
3a	158.4	
4	111.0	7.08 *d* (8.5)
5	130.7	7.68 *d* (8.5)
5a	128.6	
6	126.9	7.52 *d* (9)
7	124.1	7.36 *d* (9)
7a	130.4	
8	113.1	7.21 *s*
9	147.6	
10	148.9	
11	108.0	7.94 *s*
11a	125.6	
11b	129.9	
11c	118.1	
O-Me	56.3	4.04 *s*

(100) (calcd for $C_{17}H_{11}O_4$: 279.0657), 265 (16), 264 (74), 236 (42), 208 (19), 118 (19), 104 (31).

2-Hydroxy-1,7,8-trimethoxypyrene (**2**). Crystals from *t*-BuOMe (12 mg, only *U. lucida*), mp 183–184°. TLC: R_f 0.69; anisaldehyde: turquoise. IR ν_{max} cm^{-1}: 3368, 2919, 1509, 1456, 1428, 1407, 1307, 1292, 1228, 1200, 1168, 1109, 1076, 998, 853. UV λ_{max} nm (log ε): 252 (4.78), 271 (4.24), 282 (4.23), 305 (3.59), 320 (3.86), 334 (4.21), 350 (4.35), 375 (3.42), 396 (3.55). ^{1}H NMR: Table 3. ^{13}C NMR: Table 4. MS *m/z* (rel. int.): 308.1045 $[M]^+$ (85) (calcd for $C_{19}H_{16}O_4$: 308.1049),

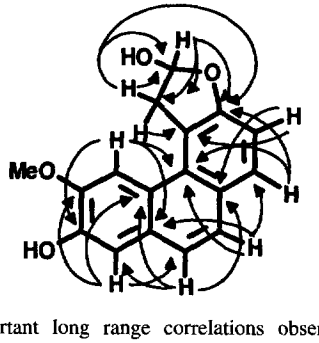


Fig. 4. Important long range correlations observed in the HMBC of compound **8**.

294 (19), 293.0810 (100) (calcd for $C_{18}H_{13}O_4$: 293.0814), 250 (25), 249 (46), 235 (29), 222 (18), 221 (52), 220 (22), 207 (43), 205 (33), 204 (16), 192 (19), 179 (17), 176 (16), 163 (23), 154 (35), 151 (27), 150 (31), 111 (15).

Chamanetin (**3**). Crystals from benzene (15 mg, only from *U. lucida*), mp 208–210° (ref. [10] mp 210–211°). TLC: R_f 0.57; anisaldehyde: orange. $[\alpha]_D$ −48° (MeOH, *c* 0.3) (ref. [10] $[\alpha]_D^{25}$ −52.5° (MeOH, *c* 1.2)). UV, IR, MS, and NMR data in agreement with lit. [10, 11].

Isochamanetin (**4**). Crystals from benzene (6 mg from *U. lucida*; 6 mg from *U. doeringii*), mp 209–212° (ref. [10] mp 215–217°). TLC: R_f 0.64; anisaldehyde: orange. $[\alpha]_D$ −11° (*c* 0.4) (ref. [10] $[\alpha]_D^{25}$ −10.5° (*c* 1.0)). UV, IR, MS, and NMR in agreement with lit. [10, 11].

Dichamanetin (**5**). Light yellow gum (213 mg from *U. lucida*; 58 mg from *U. doeringii*). TLC: R_f 0.41; anisaldehyde: orange. $[\alpha]_D$ −9° (*c* 2.3) (ref. [10] $[\alpha]_D^{25}$ −9.75° (*c* 1.2)). UV, IR, MS, and NMR data in agreement with lit. [10, 11].

Mixtures of compounds **6** and **7** were sepd either by CC on PVA 500 (MeOH) or by HPLC (Nucleosil® (Macherey–Nagel) with petrol–*t*-butylmethylether, 3:2) to yield the pure isomeric components.

Uvarinol (**6**). Light yellow gum (6 mg from *U. lucida*; 8 mg from *U. doeringii*). TLC: R_f 0.38; anisaldehyde: orange. $[\alpha]_D$ −11° (*c* 0.3) (ref. [12] $[\alpha]_D^{20}$ −16.5° (*c* 1.0)). UV, IR, MS, and NMR data in agreement with lit. [11–13].

Isouvarinol (**7**). Light yellow gum (5 mg from *U. lucida*; 10 mg from *U. doeringii*). TLC: R_f 0.37; anisaldehyde: orange. $[\alpha]_D$ −16° (*c* 0.3) (ref. [13] $[\alpha]_D^{25}$ −23.8° (*c* 1.0)). UV, IR and MS data in agreement with lit. [13]. ^{1}H NMR: Table 1. ^{13}C NMR: Table 2.

β,ε-Carotene-3,3′-diol (=*lutein*). Yellow crystals (4 mg from *U. lucida*; 3 mg from *U. doeringii*), mp 188–192° (ref. [14] mp 183°). TLC: R_f 0.45; anisaldehyde: blue. $[\alpha]_D$ +86° ($CHCl_3$, *c* 0.19) (ref. [15] $[\alpha]_D^{20}$ +62° (*c* 0.04)). UV, IR, NMR, and MS data identical with those of an authentic sample [15].

1,2-Dihydro-2,9-dihydroxy-10-methoxy-furo[2,3-a]phenanthrene (**8**). Gum (12 mg, only *U. doeringii*). TLC: R_f 0.49; anisaldehyde: blue. $[\alpha]_D$ ±0 (MeOH, *c* 0.45). IR ν_{max} cm^{-1}: 3515, 3467, 3435, 3401, 1534, 1511, 1271, 1251, 1207, 1078. UV λ_{max} nm (log ε): 210 (4.17), 238 (sh, 4.20), 258 (4.64), 284 (4.23), 289 (sh, 4.17), 299 (sh, 3.91), 312 (3.78), 327 (3.10), 343 (3.08), 362 (2.88). ^{1}H NMR: Table 5. ^{13}C NMR: Table 5. MS *m/z* (rel. int.): 282.0890 $[M]^+$ (100) (calcd for $C_{17}H_{14}O_4$: 282.0892), 253 (20), 250 (32), 222 (23), 221.0599 (75) (calcd for $C_{15}H_9O_2$: 221.0602), 193 (26), 181 (15), 165 (29), 152 (17).

1,2,7,8-Tetramethoxypyrene (**9**). Compound **1** (3 mg) (or compound **2** (2 mg)) dissolved in dry Me_2CO was treated with 1 ml MeI in the presence of K_2CO_3 for 14 hr. Filtration, evapn and CC of the residue (silica gel, $CHCl_3$–MeOH, 99:1) yielded 2 mg and 1.5 mg, respectively, of **9**. Light yellow gum. TLC: R_f 0.94;

anisaldehyde: turquoise. IR ν_{max}^{CHCl} cm^{-1}: 2937, 1598, 1299, 1088, 1005. UV λ_{max} nm (log ε): 244 (sh, 4.49), 253 (4.73), 272 (4.18), 284 (4.19), 305 (3.50), 320 (sh, 3.79), 335 (4.14), 351 (4.28), 371 (3.39), 393 (3.45). ^1H NMR: Table 3. ^{13}C NMR: Table 4. MS *m/z* (rel. int.): 322 $[M]^+$ (99), 308 (18), 307 (100), 249 (15), 248 (40), 221 (16), 161 (15).

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