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A NAPHTHOQUINONE AND A LIGNAN FROM THE WOOD OF *KIGELIA PINNATA**

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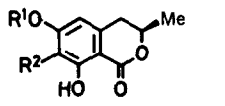
Key Word Index—*Kigelia pinnata*; Bignoniaceae; structure elucidation; naphthoquinones; lignan.

Abstract—A new naphthoquinone, kigelinone, and a new lignan, kigeliol, together with six known constituents including lapachol and dehydro-α-lapachone, were isolated from the wood of *Kigelia pinnata*. On the basis of spectral data and chemical degradations, kigelinone was characterized as 2-(1-hydroxyethyl)-8-hydroxy-naphtho[2,3-b]furano-4,9-dione and kigeliol as (2*S*, 6*S*)-bis(3,4-methylenedioxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-1*R*,5*R*-diol or its enantiomer.

INTRODUCTION

Kigelia pinnata DC., a bignoniaceous plant which is native to Africa, is found abundantly in the tropics. Its fruit is known to possess a purgative activity and its bark a healing action for ulcers. Govindachari and his colleagues isolated kigelin (**1**) and 6-methoxymellein (**2**), together with two known compounds, stigmasterol and lapachol (**3**), from the root of this plant [1]. They also isolated kigelin (**1**), β-sitosterol, 3-demethylkigelin (**4**) and ferulic acid from its bark [2].

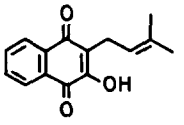
As a part of our studies on the constituents, especially naphthoquinones, of bignoniaceous plants, we have examined the wood of this plant. This paper deals with the structure elucidation of a new naphthoquinone, kigelinone (**5**), and a new lignan, kigeliol (**6**), which were isolated along with several other known compounds.



1 R^1 = Me, R^2 = OMe

2 R^1 = Me, R^2 = H

4 R^1 = H, R^2 = OMe



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RESULTS AND DISCUSSION

The benzene extract from the wood of *K. pinnata*, collected in Taiwan, was fractionated by column chromatography (CC) on silica gel, and the fraction obtained chromatographed on various absorbents to give eight compounds.

Structure of kigelinone (**5**)

Kigelinone (**5**) was isolated as yellow needles, $C_{14}H_{10}O_5$, mp 180–181°, $[\alpha]_D^{24}$ −17.5° ($CHCl_3$). Its UV and IR spectra [λ_{max} (log ε) 235 (3.91), 248 (4.01), 300 (3.36) and 398 nm (3.25); ν_{max} 1660, 1630, 1590, 1570 and 1525 cm^{-1}] indicated that it was a 1,4-naphthoquinone. In particular, the bands at 1660 and 1630 cm^{-1} in the IR spectrum suggested that it was a 5-hydroxy-1,4-naphthoquinone (juglone-type naphthoquinone) [3]. This assumption was supported by its ^1H NMR spectrum, which showed a sharp singlet at δ 12.16 for a chelated phenolic hydroxy proton and an ABX pattern in the aromatic proton region [δ_A 7.76 (*dd*, J_{AX} = 1.6 Hz, J_{AB} = 7.5 Hz), δ_B 7.60 (*dd*, J_{BX} = 8.0 Hz, J_{AB} = 7.5 Hz), δ_X 7.26 (*dd*, J_{AX} = 1.6 Hz, J_{BX} = 8.0 Hz)] for three aromatic protons. Therefore, it followed that kigelinone (**5**) possessed the partial structure **7**.

In addition to the above-mentioned signals, the ^1H NMR spectrum of kigelinone showed a doublet at δ 1.65 (J = 6.5 Hz) for a secondary methyl group, a broad singlet at δ 2.23 (lost on treatment with D_2O) for an alcoholic hydroxy proton, a double quartet at δ 5.05 (J = 1.0 and 6.5 Hz) for a proton on the hydroxy-bearing carbon and a doublet at δ 6.83 (J = 1.0 Hz) for an olefinic proton in a dienone system. A spin decoupling experiment revealed long-range coupling (J = 1.0 Hz) between the latter two protons. Acetylation of **5** in the usual way gave a diacetate (**8**) whose ^1H NMR spectrum showed, besides two singlets at δ 2.10 and 2.46 for an alcoholic and a phenolic acetoxy group respectively, a doublet at δ 1.67 (J = 6.5 Hz) for a secondary methyl group, a broad quartet at δ 6.02 (J = 6.5 Hz) for a methine proton on the acetoxy-bearing carbon and a broad singlet at δ 6.82 for an olefinic proton in a dienone system. Thus, the comparison of the ^1H NMR spectrum of **5** with that of **8** suggested that kigelinone (**5**) possessed the partial structure **9**.

The remaining oxygen of **5** must be in an ethereal linkage, since no characteristic band for it was observed in

* Part 17 in the series "Quinones and Related Compounds in Higher Plants". For Part 16, see Inoue, K., Chen, C.-C. and Inouye, H. (1980) *J. Chem. Soc. Perkin Trans.* 1 (accepted).

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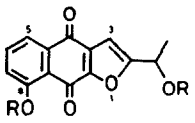
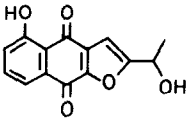
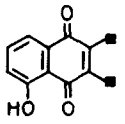
the IR spectrum of this compound and, furthermore, it was resistant to acetylation. In view of the above partial structures **7** and **9**, it was therefore concluded that the oxygen was in a furan ring. Accordingly, the structure **5** or **5a** was assigned to kigelinone.



5 R=H
8 R=Ac



5a



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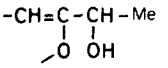

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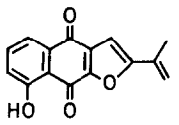

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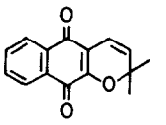

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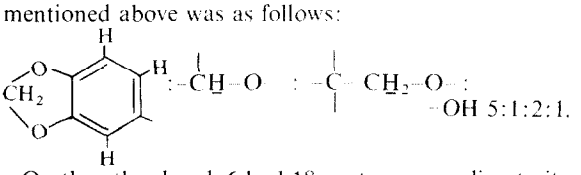
Recently, we characterized one of the naphthoquinone constituents of the callus tissues of *Catalpa ovata* as 2-isopropenyl-8-hydroxyfurano-1,4-naphthoquinone (**10**) [4]. The chemical shift of its hydroxy proton on C-8 (δ 12.10) coincided with that of the corresponding proton of kigelinone.* Therefore for the structure of kigelinone, formula **5** was preferable to **5a**. On this basis, the structure of kigelinone was concluded to be 2-(1-hydroxyethyl)-8-hydroxynaphtho[2,3-b]furano-4,9-dione, though the absolute configuration of the hydroxy group in the side-chain could not be defined because of the scarcity of the substance.

In view of the co-occurrence of lapachol (**3**) and dehydro-α-lapachone (**11**) (see below) in this plant, **5** is thought to be one of the congeners of prenyl-1,4-naphthoquinone which has lost a methyl group during the biosynthetic process.

Structure of kigeliol (**6**)

Kigeliol (**6**) was obtained as colourless needles, $C_{20}H_{18}O_8$, mp 150–151°, $[\alpha]_D^{24}$ −34.6° ($CHCl_3$). Its IR spectrum showed the presence of hydroxy groups [3450 (sh) and 3340 cm^{-1}] and benzene rings (1607 cm^{-1}). Furthermore, its UV [λ_{max} (log ε) 238 (3.96) and 286 nm (3.83)] and ^1H NMR spectra [δ 5.95 (2H, *s*, $-OCH_2O-$) and 6.77 6.97 (3H, *m*, 3 aromatic protons)] were extremely similar to those of piperonyl alcohol, suggesting that kigeliol (**6**) contained 3,4-methylenedioxyphenyl moieties.

The ^1H NMR spectrum of **6** showed, in addition to the above signals, a sharp singlet at δ 2.52 for hydroxy protons (lost on treatment with D_2O). **6** could neither be acetylated in the usual way with Ac_2O–pyridine nor oxidized with Jones reagent. However, acetylation of **6** with Ac_2O–triethylamine in the presence of 4-dimethylaminopyridine gave an acetate (**12**), indicating the tertiary character of its hydroxy groups. Although the IR spectrum of **6** showed a hydroxyl absorption, it did not show any absorptions characteristic of a carbonyl group. Thus, all the remaining six oxygen functions were thought to be involved in ethereal linkages, including those of the methylenedioxy groups in the piperonyl moieties. Furthermore, the ^1H NMR spectrum of **6** showed, besides the above-mentioned signals, two singlets at δ 4.97 and 4.08 assignable to ϕ–$\underset{|}{C}H$–O– and –$\underset{|}{C}H_2$–O–, respectively. The ratio of the intensities of signals mentioned above was as follows:

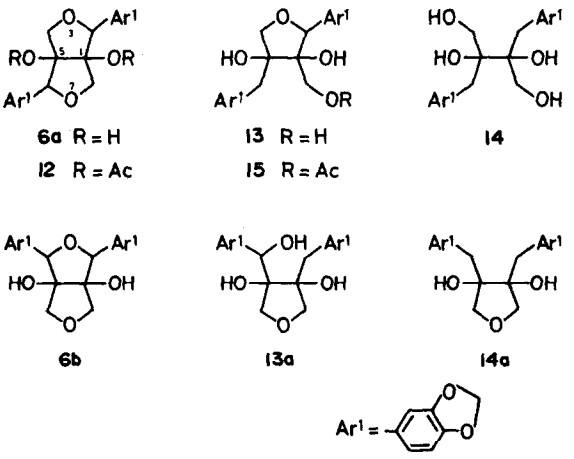


On the other hand, **6** had 18 protons according to its MS (*m/z* 368 M^+) and composition ($C_{20}H_{18}O_8$). It followed, therefore, that **6** had a symmetrical structure consisting of the above characterized moieties. This was also corroborated by the appearance of just 10 peaks in the proton-noise-decoupled ^{13}C NMR spectrum of **6** (see Table 2). Thus, as regards the structure of kigeliol (**6**) either of two formulae, **6a** and **6b**, were possible. The problem concerning which of the two structures should be assigned to kigeliol was solved from the comparison of the structures of two hydrogenolysis products of **6**. Hydrogenolysis of kigeliol was expected to afford either the two products **13** and **14**, if it had the structure **6a**, or **13a** and **14a**, if it was **6b**. In practice, hydrogenolysis of kigeliol in MeOH with 10% Pd–C gave rise to dihydrokigeliol (**13**) and tetrahydrokigeliol (**14**). The main product **13** was obtained as colourless needles, mp 115–116°, showing a strong IR band of hydroxy groups at 3500 cm^{-1}. Its ^1H NMR spectrum contained, in addition to a singlet at δ 5.91 for the methylene protons of the two methylenedioxy groups and a multiplet at δ 6.65–6.93 for six aromatic protons, a broad signal at δ 1.83–3.17 for three hydroxy protons (lost on treatment with D_2O), an AB quartet for ϕ–$\underset{|}{C}H_2$–$\underset{|}{C}$– at δ 2.68 and 2.97 (each *d*, J = 13.5 Hz), an AB quartet for $\underset{|}{C}$–CH_2–O– at δ 3.66 and 3.88 (each *d*, J = 9.0 Hz), an overlapping signal for methylene protons on a primary hydroxy-bearing carbon at δ 3.62–3.85 and a singlet for ϕ–$\underset{|}{C}H$–$\underset{|}{C}$– at δ 4.87. On acetylation, **13** gave a monoacetate (**15**) whose ^1H NMR spectrum showed a singlet for an acetoxy group at δ 2.08, two broad singlets for two hydroxy protons at δ 2.70 and 2.86 and a broad singlet for methylene protons on the acetoxy-bearing carbon at δ 4.32. These data implied that

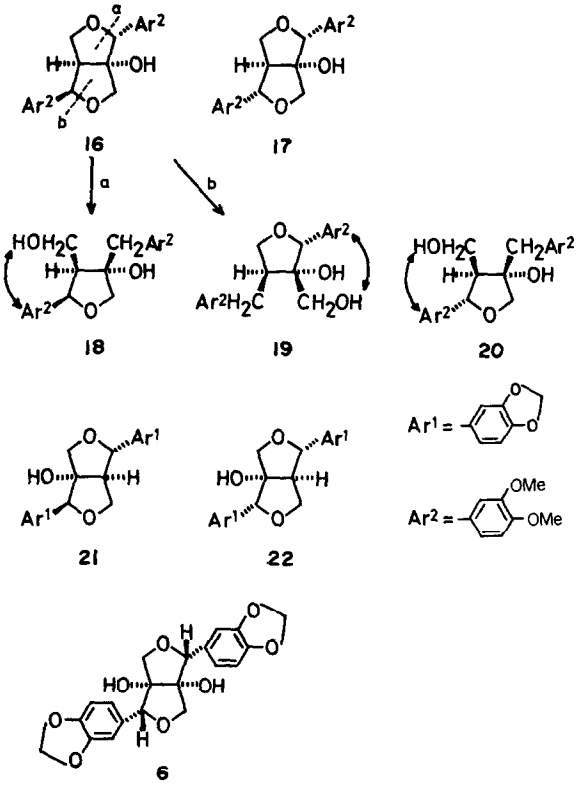
* Musgrave *et al.* reported an empirical rule concerning the effects of several substituents on the chemical shift of the *peri* hydroxy group in juglone-type naphthoquinones [5], and we extended this rule to α-lapachones and dehydro-iso-α-lapachones hydroxylated in *peri* positions [6]. Although this rule cannot be unrestrictedly applied to furanonaphthoquinones hydroxylated in the *peri* position, it seems likely that there is a significant difference between chemical shifts of phenolic hydroxy protons in compounds of both types **5** and **5a**.

one of the three hydroxy groups of **13** was primary and the remaining two were tertiary. Therefore, the major product of hydrogenolysis was dihydrokigeliol (**13**) which was formed by hydrogenolytic cleavage of one tetrahydrofuran ring of **6**.

The minor product (**14**) was obtained as colourless prisms, $C_{20}H_{22}O_8$, mp 210–211°. Its IR spectrum showed a strong band at 3500 cm^{-1} due to hydroxy groups. The ^1H NMR spectrum exhibited an AB quartet for a pair of benzylic methylene protons at δ 2.68 and 2.97 (each *d*, J = 13.5 Hz), an AB quartet for a pair of methylene protons on the primary hydroxy-bearing carbons at δ 4.00 and 4.24 (each *d*, J = 11.5 Hz) and a broad signal for four hydroxy protons at δ 5.00–5.67 (lost on treatment with D_2O). In addition, the ^1H NMR spectrum of **14**, unlike those of **6**, **13** and **15**, indicated a typical ABX pattern in the aromatic region [δ_A 7.34 (*d*, J = 1.5 Hz), δ_B 7.16 (*d*, J = 1.5 and 8.0 Hz), δ_X 6.84 (*d*, J = 8.0 Hz)], supporting the above-mentioned substitution pattern of the phenyl group. These spectral data showed that tetrahydrokigeliol possessed a symmetrical structure (**14**) formed through the hydrogenolytic cleavage of the remaining tetrahydrofuran ring in dihydrokigeliol (**13**). The presence of a primary hydroxy group in dihydrokigeliol and two of the same groups in tetrahydrokigeliol rules out the possibility of having structures **13a** and **14a** for these compounds. These results showed that the structure of kigeliol (**6**) was 2,6-bis(3,4-methylenedioxyphenyl)-3,7-dioxabicyclo-[3.3.0]octan-1,5-diol.



Next, the relative stereochemistry of kigeliol (**6**) was examined. Birch *et al.* [7] elucidated the relative stereostructures of gmelinol (**16**) and its stereoisomer isogmelinol (**17**), constituents of an Australian verbenaceous plant *Gmelia leichlardtii*, by comparing the ^1H NMR spectra of two partial reduction products of the former, dihydrogmelinol-I (**18**) and dihydrogmelinol-II (**19**) with that of olivil dimethyl ether (**20**) [8] with defined absolute structure. Since dihydrokigeliol (**13**) has a similar structure to these compounds, we attempted to establish the relative configuration of kigeliol (**6**) by comparing the ^1H NMR spectrum of **13** with those of **18**, **19** and **20**. The chemical shifts of C-2 protons and hydroxy protons of the C-3 hydroxymethyl groups in the ^1H NMR spectra of these compounds, which varied significantly depending upon the relative configuration of the C-2 aryl group and C-3 hydroxymethyl group, are shown in Table



1. As can be seen from the examples given, the C-2 protons appeared at a higher field, when both groups assumed *trans* configuration, and the hydroxy protons of the C-3 hydroxymethyl groups appeared at a higher field when both groups were in *cis* orientation. The chemical shifts of the corresponding protons of dihydrokigeliol (**13**) were in excellent accordance with those of dihydrogmelinol-II (**19**) and olivil dimethyl ether (**20**) having both *trans*-oriented groups.

Both aryl groups in kigeliol (**6**) were assumed to have the same configuration from the following three facts: (1) in the ^1H NMR spectrum of **6**, two benzylic protons appeared as a singlet with the identical chemical shift. (2) In the noise-decoupled ^{13}C NMR spectrum of **6**, both benzylic carbons appeared as a singlet. (3) Hydrogenolysis of **6** gave **13** as the sole dihydro-derivative. Furthermore, in the 3,7-dioxabicyclo[3.3.0]octane system, which comprises the structure of kigeliol (**6**), both hydroxy groups at C-1 and C-5 positions can only assume the *cis* and axial configuration. Accordingly, it followed that both aryl groups in kigeliol (**6**) must have the equatorial configuration. This inference was also supported by the ^{13}C NMR spectrum of **6**. Recently, Pelter *et al.* [9] reported that, in the ^{13}C NMR spectra of lignans having the 2,6-diaryl-3,7-dioxabicyclo-[3.3.0]octane skeleton, the signal of the carbon bearing an equatorial aryl group (δ 85.61–87.71) generally appears in a lower field than that of the carbon bearing an axial aryl group (δ 81.11–83.96). The appearance of the signal of C-2 and C-6 at δ 86.91 in the ^{13}C NMR spectrum of **6**, therefore, suggested that both aryl groups of this compound should assume the equatorial position. Thus, all the results mentioned above allowed us to assign the structure of kigeliol to 2*S*,6*S*-bis(3,4-methylenedioxyphenyl)-3,7-

Table 1. ^{1}H NMR data of C-2 proton and hydroxy proton of the C-3 hydroxymethyl group in compounds **13**, **18**, **19** and **20** (60 MHz, $CDCl_3$, TMS as int. standard)

	Configuration between C-2 aryl group and C-3 hydroxymethyl group	C-2 proton	OH of C-3 CH_2OH group
Dihydrokigeliol (**13**)	*trans*	4.87 *s*	2.56
Dihydrogmelinol-I (**18**)	*cis*	5.55 *d*	1.42
Dihydrogmelinol-II (**19**)	*trans*	4.86 *d*	—
Olivil dimethyl ether (**20**)	*trans*	4.72 *d*	2.45

dioxabicyclo[3.3.0]octan-1*R*,5*R*-diol (**6**) or its enantiomer and those of its four derivatives to formulae **12**, **13**, **14** and **15** with the corresponding stereochemistry. Kigeliol is the first sesamin-type lignan having two tertiary hydroxy groups at C-1 and C-5 positions, respectively. As far as we know, sesamin-type lignans have not yet been found in the bignoniaceous plants. Paulownin (**21**) and isopaulownin (**22**) [10] of the same type, however, have been isolated from *Paulownia tomentosa* (Thunb.) Sted. The problem of its taxonomical position, whether it belongs to Bignoniaceae or Scrophulariaceae, is still a subject of controversy.

Besides the above-mentioned new compounds, two known prenylnaphthoquinones, lapachol (**3**) and dehydro-α-lapachone (**11**), and four known non-quinonoid constituents, kigelin (**2**), β-sitosterol, triacontanoic acid and vanillin were isolated from the wood of *K. pinnata* and identified by mixed mp and comparisons of spectra with authentic specimens.

Finally, the seasonal fluctuation of the constituents was also examined on branches cut from the same tree in January, April, June and October, respectively. The results showed that the naphthoquinones increased between October and January and significantly decreased between April and June, and further kigeliol (**6**) increased between January and April and decreased in October to a scarcely detectable level, while the content of kigelin and β-sitosterol did not change significantly throughout the year.

EXPERIMENTAL

Unless otherwise stated, ^{1}H NMR spectra were determined at 60 MHz and ^{13}C NMR spectra at 25 MHz in $CDCl_3$ with TMS as int. standard. MS were obtained on a direct inlet operating at 70 eV. GLC was carried out using glass columns packed with 3% silicone OV-1 on Gas Chrom Q and 1.5% silicone OV-17 on Shimalite W. Separations by CC were carried out with Mallinckrodt Si gel AR-100, Sephadex LH-20 and acetylated polyamide [prepared through acetylation of Wako polyamide C-200 (100 g) with Ac_2O (400 ml) and Py (400 ml)]. TLC was performed on Merck Si gel 60 GF-254 and spots were detected by irradiation with UV light, exposure to I_2 vapour and spraying with anisaldehyde–H_2SO_4 reagent followed by heating. Prep. TLC was performed on Merck Si gel 60 PF-254 and bands were detected by irradiation with UV light.

Table 2. ^{13}C NMR spectral data of **6**, (25 MHz, $CDCl_3$, TMS as internal standard)

Carbon No.	
1,5	87.60 *s*
2,6	86.89 *d*
4,8	76.38 *t*
1′,1″	129.30 *s*
2′,2″	107.61 *d**
3′,3″	147.72 *s*†
4′,4″	147.95 *s*†
5′,5″	108.32 *d**
6′,6″	120.30 *d*
$-OCH_2O-$	101.16 *t*

* Interchangeable.
† Interchangeable.

Plant material. Kigelia pinnata DC. was collected at Heng Chun Tropical Botanical Garden and a voucher specimen, herbarium H. Inouye Bignoniaceae 2, deposited at the Department of Botany, Faculty of Science, Kyoto University

Isolation of constituents. The wood (8.5 kg) of *K. pinnata* collected in Jan. was dried, cut into pieces and extracted with C_6H_6 (20 l. × 3) under reflux. The concd extract (33 g) was chromatographed on Si gel (453 g) using 0% (1.6 l.), 2% (2 l.), 4% (4 l.), 6% (6 l.), 8% (1.5 l.), 10% (0.7 l.), 12% (2 l.), 14% (0.5 l.), 16% (1 l.) and 18% (0.5 l.) EtOAc in C_6H_6 as developing solvent (chr. 1). 200-ml fractions were collected.

Chr-1-1 (*fractions* 13–19). The residue (455 mg) obtained on concn was recryst. from EtOH to give colourless needles (210 mg), mp 82–83°, of triacontanoic acid (mps, and direct comparison of IR and ^{1}H NMR spectra with those of authentic sample).

Chr-1-2 (*fractions* 20–24). The residue (900 mg) was rechromatographed on Si gel (40 g) with C_6H_6 (20-ml fractions). The residue (24 mg) obtained from chr-1-2-1 (fractions 15–20) was purified by prep. TLC (C_6H_6–EtOAc, 7:3). The band around R_f 0.52 afforded red-orange pillars (5 mg), mp 143°. UV λ_{max}^{MeOH} nm (log ε): 253 (4.24), 282 (4.16), 338 (3.26); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1635 (sh), 1625, 1585, 1565, 870, 790; ^{1}H NMR: δ 1.55 [6 H, *s*, $(CH_3)_2C-O-$], 5.72 (1 H, *d*, J = 10.0 Hz, olefinic H), 6.65 (1 H, *d*, J = 10.0 Hz, olefinic H), 7.58–8.18 (4 H, A_2B_2 pattern, 4 × arom. H). This substance was identified as dehydro-α-lapachone (**11**) (mmp, and direct comparison of IR and ^{1}H NMR spectra with those of authentic sample). The residue (36 mg) obtained from chr-1-2-2 (fractions 25–31) was recrystallized from MeOH to give red-orange scales (24 mg), mp 141–142°, UV λ_{max}^{MeOH} nm (log ε): 253 (4.39), 280 (4.27), 331 (3.51); IR ν_{max}^{Nujol} cm^{-1}: 3350, 1655, 1635, 1590, 840, 720; ^{1}H NMR: δ 1.70 and 1.80 [each 3 H, *s* (*br*), $(CH_3)_2C=C<$], 3.31 [2 H, *d* (*br*), J = 8.0 Hz, $-CH_2CH=C<$], 5.23 [1 H, *t* (*br*), J = 8.0 Hz, $-CH_2CH=C<$], 7.40 [1 H, *s* (*br*), –OH, lost on treatment with D_2O], 7.50–8.23 (4 H, A_2B_2 pattern, 4 × arom. H). This substance was identified as lapachol (**3**) (mmp, and direct comparison of IR and ^{1}H NMR spectra with those of authentic sample).

Chr-1-3 (*fractions* 27–30). The residue (2.1 g) was recryst. from EtOH to give colourless needles (1.7 g), mp 138–139° which was identical with β-sitosterol (mps, IR and ^{1}H NMR spectra).

Chr-1-4 (*fractions* 70–73). The residue (700 mg) was rechromatographed on Si gel (20 g) with C_6H_6 (20-ml fractions). The residue from chr-1-4-1 (fractions 20–25) was recryst. from MeOH to give kigelin (**1**) (270 mg) as colourless needles, mp 144.5–146°, $[\alpha]_D^{24}$ −81.0° (*c* 1.0, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 221 (4.47), 230 (4.44), 275 (4.32), 312 (3.88); IR ν_{max}^{Nujol} cm^{-1}: 1650, 1610, 1600, 1570, 1500; ^1H NMR: δ 1.52 (3 H, *d*, *J* = 6.0 Hz, –O–CH(–CH₃)–), 2.88 [2 H, *d* (*br*), *J* = 7.5 Hz, φ–CH₂–CH(–O–)–], 3.88 and 3.98 (each 3 H, *s*, OMe), 4.69 (1 H, *m*, –CH₂CHMe) 6.32 [1 H, *s* (*br*), arom. H], 11.18 (1 H, *s*, –OH, lost on treatment with D_2O); MS *m/z*: 238 (M^+). (Found: C, 60.74; H, 6.21. Calc. for $C_{12}H_{14}O_5$: C, 60.56; H, 5.93%.) These data were in good agreement with those reported for kigelin [1].

Chr-1-5 (*fractions* 83–88). The residue (1.1 g) was rechromatographed on Si gel (30 g) with C_6H_6–EtOAc (49:1) as eluant (20-ml fractions). The residue (60 mg) from chr-1-5-1 (fractions 18–26) was chromatographed on Sephadex LH-20 (40 ml) using $CHCl_3$–MeOH–*n*-heptane (1:1:2) as eluant and 3 ml fractions were collected. The residue from fractions 13–20 was recrystallized from EtOH to give kigelinone (**5**) (32 mg) as yellow needles. (MS: M^+ 258.0531. $C_{14}H_{10}O_5$ requires: 258.0528.)

Chr-1-6 (*fractions* 90–99). The residue (1.2 g) was rechromatographed on Si gel (40 g using C_6H_6–EtOAc (19:1) as eluant and 30-ml fractions were collected. The residue (650 mg) from chr-1-6-1 (fractions 24–33) was recrystallized from C_6H_6–EtOAc to give kigeliol (**6**) (240 mg) as colourless needles. (Found C, 62.22; H, 4.51. $C_{22}H_{18}O_8$ requires: C, 62.17; H, 4.69%.)

The wood (10 kg) collected in April was subjected to the same isolation procedures as described above to give **1** (120 mg, 0.0012%), β-sitosterol (1.33 g, 0.013%), **5** (6 mg, 0.00006%) and **6** (370 mg, 0.0037%). The wood (5.8 kg) collected in June gave **1** (130 mg, 0.002%), β-sitosterol (1.60 g, 0.03%), vanillin (11 mg, 0.0002%), **5** (5 mg, 0.00009%) and **6** (92 mg, 0.0016%). Finally, the wood (7.0 kg) collected in Oct. gave **1** (650 mg, 0.009%), β-sitosterol (1.90 g, 0.027%), triacontanoic acid (95 mg, 0.0014%), **3** (19 mg, 0.003%), **5** (7 mg, 0.0001%) and **11** (19 mg, 0.0003%).

Acetylation of kigelinone (**5**). **5** (4 mg) was acetylated with Ac_2O (0.04 ml) and pyridine (0.04 ml). The usual work-up gave a residue which was recrystallized from MeOH to afford the diacetate **8** (3.5 mg) as orange needles, mp 140–142°. UV λ_{max}^{MeOH} nm (log ε): 248 (4.41), 290 (3.77) and 323 (3.70); ^1H NMR (100 MHz): δ 1.67 (3 H, *d*, *J* = 6.5 Hz, –O–CH(–CH₃)–), 2.10 (3 H, *s*, alcoholic OAc), 2.46 (3 H, *s*, phenolic OAc), 6.02 (1 H, *q* (*br*), *J* = 6.5 Hz, AcO–CH(–Me)–), 6.82 [1 H, *s* (*br*), 3-H], 7.36 (1 H, *dd*, *J* = 8.0 and 2.0 Hz, 7-H), 7.76 (1 H, *t*, *J* = 8.0 Hz, 6-H) and 8.20 (1 H, *dd*, *J* = 8.0 and 2.0 Hz, 5-H). (MS: M^+ 342.0842. $C_{18}H_{14}O_7$ requires: 342.0739.)

Acetylation of kigeliol (**6**). Ac_2O (0.4 ml), triethylamine (0.05 ml) and 4-dimethylaminopyridine (1 mg) was added to a soln of **6** (23 mg) in dry CH_2Cl_2 (2 ml) and the mixture allowed to stand at room temp. for 40 hr. The solution was poured into ice–H_2O, and after separation of the CH_2Cl_2 layer, the aq. layer was extracted with $CHCl_3$ (15 ml × 2). The combined organic layers were washed successively with 1 N HCl, satd $NaHCO_3$ and H_2O, dried and concd *in vacuo*. The residue (31 mg) was purified by PLC (C_6H_6–EtOAc, 7:3). The band around R_f 0.56 afforded a crystalline residue which was recrystallized from MeOH to give the diacetate **12** as colourless needles, mp 127–129°. IR ν_{max}^{Nujol} cm^{-1}: 1740, 1605, 1490, 865, 815; ^1H NMR: δ 1.86 (6 H, *s*, 2 × OAc), 4.39 (4 H, *s*, 2 –O–CH₂–C(–)–), 5.15 (2 H, *s*, 2 × φ–O–CH(–C–)–), 5.94 (4 H, *s*, 2 × –O–CH₂–O–) and 6.77–7.00 (6 H, *m*, 6 × arom. H). (Found: C, 61.10; H, 4.82. $C_{24}H_{22}O_{10}$ requires: C, 61.27; H, 4.71%.)

Hydrogenolysis of kigeliol (**6**). **6** (300 mg) in EtOH (30 ml) was hydrogenated at room temp. and atm pres. in the presence of the catalyst prepared from 10% $PdCl_2$ (3.8 ml) and activated charcoal (Darco 60) (300 mg). The catalyst was filtered off and the filtrate was concd *in vacuo* to give a residue (240 mg), which was purified by prep. TLC (C_6H_6–EtOAc, 4:1). Of the resulting three bands (R_f 0.80, 0.41 and 0.25), the band around R_f 0.80 afforded the starting material (**6**) (110 mg). The band around R_f 0.41 yielded a residue (140 mg) which was recrystallized from MeOH to give dihydrokigeliol (**13**) as colourless needles, mp 115–116°. UV λ_{max}^{MeOH} nm (log ε): 237 (3.36), 287 (3.30); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1600, 1480, 860. (Found: C, 61.73; H, 5.26. $C_{20}H_{20}O_8$ requires: C, 61.85; H, 5.19%.) Finally the band around R_f 0.25 afforded a residue (24 mg), which was recrystallized from MeOH to give tetrahydrokigeliol (**14**) as colourless prisms, mp 210–211°. IR ν_{max}^{Nujol} cm^{-1}: 3370, 3270, 1600, 1485, 910, 860, 815. (MS: M^+ 390.1315. $C_{20}H_{22}O_8$ requires: 390.1315.)

Acetylation of dihydrokigeliol (**13**). **13** (30 mg) was acetylated with Ac_2O and pyridine (each 0.3 ml). The usual work-up afforded a residue (34 mg), which was recrystallized from MeOH to give the monoacetate **15** (28 mg) as colourless needles, mp 115–116°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1740, 1610, 1500, 1490, 935, 865, 815; ^1H NMR: δ 2.08 (3 H, *s*, OAc), 2.70 (1 H, *s*, –OH, lost on treatment with D_2O), 2.70 and 2.97 (2 H, each *d*, *J* = 14.0 Hz, –CH₂–C(–)–), 2.86 (1 H, *s*, –OH, lost on treatment with D_2O), 3.73 and 3.93 (2 H, each *d*, *J* = 9.0 Hz, –C(–OH)–CH₂–O–), 4.32 [2 H, *s* (*br*), –CH₂–OAc], 4.98 (1 H, *s*, φ–CH(–C–)–), 5.94 (4 H, *s*, 2 × –O–CH₂–O), 6.70–6.94 (6 H, *m*, 6 × arom. H). (MS: M^+ 430.1279. $C_{22}H_{22}O_9$ requires: 430.1264.)

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