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LIGNANS AND NEOLIGNANS FROM *BUDDLEJA DAVIDII*

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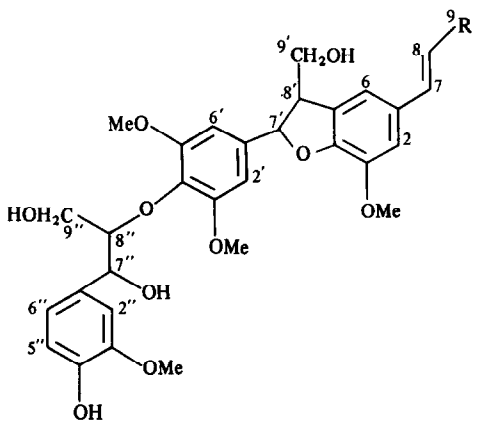
Key Word Index—*Buddleja davidii*; Loganiaceae; stems; lignans; neolignans; dihydrobenzofurans; furofurans; buddlenols.

Abstract—A methanolic extract of *Buddleja davidii* stem yielded the known compounds coniferaldehyde, balanophonin and syringaresinol, and six novel compounds which were characterized as arylglycerol-substituted lignans and neolignans. These have been named buddlenols A–F.

INTRODUCTION

The genus *Buddleja* has widespread use in folk medicine [1]. *B. davidii* Franchet, although indigenous to China, has become widely naturalized in the temperate regions of the world. Previous chemical investigations have shown the presence of flavonoids and iridoids [2] and more recently piscicidal sesquiterpenes have been isolated from the roots [3, 4]. Taxonomically the genus is usually included in the Loganiaceae although there are some grounds for classifying it as a separate family. The Loganiaceae is well-known as a source of indole alkaloids and the work reported here originated as an investigation into the possibility of the presence of alkaloids in *Buddelja*. Screening procedures have, somewhat equivocally, suggested the presence of alkaloids in *B. davidii* [5, 6] whilst other species have been reported to contain easily detectable amounts [7, 8].

This paper reports the isolation of Dragendorff-positive compounds from *B. davidii* and their characterization, not as alkaloidal substances, but as phenolic phenylpropide derivatives. Nine compounds have so far been isolated and identified. These are the known compounds coniferaldehyde (**1**), balanophonin (**2**) and syringaresinol (**3**) and six novel compounds containing an arylglycerol portion attached to either a dihydrobenzofuran neolignan (**4**, **5**) or a furofuran lignan (**6–9**).



R

4 CHO Buddlenol A

5 CH_2OH Buddlenol B

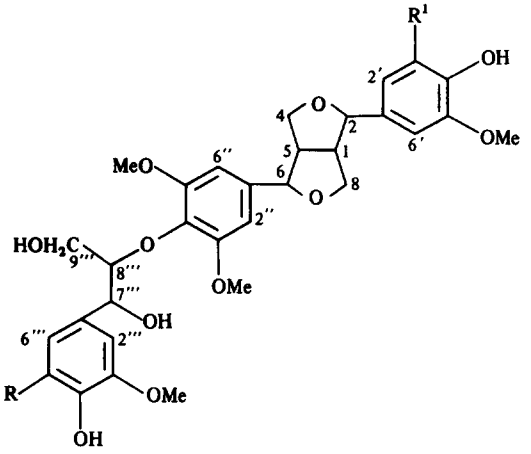
RESULTS AND DISCUSSION

A compound giving a blue colour after heating was identified as coniferaldehyde (**1**) as it agreed in all respects with published data. Another substance giving a blue colour was identified as balanophonin (**2**) by comparison of spectral data [9] since no authentic compound was available from the authors. A compound giving a pink-red colour after spraying was identified as syringaresinol (**3**) [10] by comparison with published spectral data.

Buddlenol A (**4**)

The UV and ^{1}H NMR spectra of buddlenol A exhibited features similar to those in **1** and **2**. The peaks at 276 and 334 nm in the UV spectrum can be assigned to the aromatic–propenal side-chain conjugated system. The signals at δ9.65 (CHO), 7.42 (–CH=CH–CHO) and 6.61 (–CH=CH–CHO) in the ^{1}H NMR spectrum were assigned by decoupling experiments.

The mass spectrum shows a very small $[M]^+$ peak at *m/z* 582 and the major peaks are at *m/z* 386, 368, 210, 180, 151 and 137. The *m/z* 137 and 151 peaks are characteristic of a coniferyl (4OH–3MeO–phenyl) residue in lignans [11]. The *m/z* 180 peak can be assigned to a coniferyl alcohol residue. The $[M]^+$ of 582 implies that the molecule is comprised of three phenylpropide units and from the above it is likely that one end of the molecule is a phenyl propenal. The large peak at *m/z* 386 and the corresponding ones at *m/z* 368 and 356 imply the presence of a $-CH_2OH$ group in this fragment and its mass suggests that it consists of two phenylpropide units such as does balanophonin (**2**), which, however, has a mass of 356, i.e. 30 less than the peak under consideration. An extra methoxyl group may account for this.



	R	R^1	
6	H	OMe	Buddlenol C
7	OMe	OMe	Buddlenol D
8	H	H	Buddlenol E
9	OMe	H	Buddlenol F

The ^{1}H NMR spectrum shows signals indicating the presence of four aromatic methoxyl groups and seven aromatic protons. This further increases the possibility that **4** consists of three coniferyl phenylpropide residues. The 1H doublet at δ5.67 can be assigned to a CH adjacent to an aromatic ring and the oxygen atom of the ether linkage in a dihydrobenzofuran. A similar signal is seen in the ^{1}H NMR spectrum of balanophonin (**2**) and related compounds. The ill-defined 1H doublet at δ5.00 moves downfield to 6.04 in the acetylated compound and resolves into two doublets in an approximately 3:1 ratio. A similar effect was observed in the spectra of such compounds as carinatidiol (**10**) [12] and the dilignols isolated from the leaves of various coniferous plants [13, 15]. The signal can be attributed to H-1 of a 1-aryl glycerol linked via an ether bridge from C-2 to a phenylpropide residue. The two doublets observed are due to the substance isolated being a mixture of the *threo* and *erythro* isomers in the glycerol portion of the molecule, the *threo* isomer being the major one present.

The ^{13}C NMR spectrum of **4**-acetate (Table 1) shows signals at δ73.9 and 81.0 which agree with this interpretation. Similarly, peaks are present which can be attributed to the non-aromatic C atoms of a dihydrobenzofuran ring. The signal at δ103.1 must be due to the 2,6-CH atoms in a 3,4,5-OR phenyl and this is seen in the middle aromatic ring of the structure proposed (**4**). The extra methoxyl group in the part of the molecule corresponding to balanophonin also explains the *m/z* 386 fragment mentioned above.

The ^{1}H NMR spectrum of **4**-acetate shows that four acetates are present, one (δ2.30) being attached to an aromatic ring and the other three being aliphatic. The presence of one phenolic hydroxyl and three aliphatic hydroxyl groups in the parent compound is thus indicated.

It is therefore likely that buddlenol A consists of three phenylpropides linked together, one terminal unit being a phenylpropenal and the other a phenylglycerol. These are joined by the non-aromatic portion of a dihydrobenzofuran ring and an ether bridge respectively to the third unit which forms the central part of the molecule. Since cleavage upon electron impact occurs most easily at the ether bridge, it is suggested that the major peaks at *m/z* 386 and 180 are formed as shown in Scheme 1. As mentioned above, the *m/z* peaks at 180, 151 and 137 suggest that the substituent on the glycerol is 4-OH, 3-OMe phenyl.

Buddlenol A is therefore considered to have the structure **4**.

Table 1. ^{13}C NMR data of the acetates of buddlenols A and B (20 MHz, $CDCl_3$, TMS as internal standard)

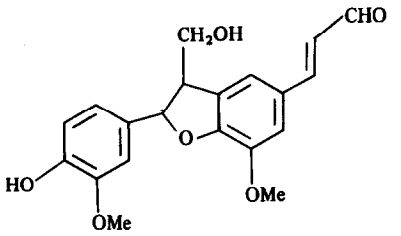
	Buddlenol A acetate		Buddlenol B acetate	
C	Observed	Calculated	Observed	Calculated
1	127.5	127.8	127.5	127.8
2	111.5	112.3	111.5	112.3
3	141.5	144.4	141.5	144.4
4	150.8	151.2	150.8	151.2
5	131.7	132.0	131.7	132.0
6	119.1	118.0	119.1	118.0
7	153.5	152.9	134.3	134.8
8	126.8	126.0	127.5	127.4
9	193.4	193.2	65.3	63.8
1′	131.7	132.1	131.7	132.1
2′	103.1	102.9	103.1	102.9
3′	152.9	152.1	152.9	152.1
4′	136.1	136.1	136.1	136.1
5′	152.9	152.1	152.9	152.1
6′	102.9	103.1	102.9	103.1
7′	88.6	88.8	88.6	88.8
8′	50.5	50.9	50.5	50.9
9′	65.2	66.1	65.2	66.1
1″	130.7	131.6	130.7	131.6
2″	110.6	108.6	110.6	108.6
3″	148.3	146.5	148.3	146.5
4″	144.5	145.6	144.5	145.6
5″	115.3	114.3	115.3	114.3
6″	121.3	119.1	121.3	119.1
7″	73.9	74.0	73.9	74.0
8″	81.0	82.5	81.0	82.5
9″	63.7	64.0	63.7	64.0
OMe	56.1	56.0	56.1	56.0

Assignments were made with the aid of the DEPT spectra for each compound.

Buddlenol B (**5**)

Buddlenol B gives a mass spectrum very similar to that of buddlenol A except that the peaks at *m/z* 584 $[M]^+$, 388, 370 and 358 are greater by 2 amu than the corresponding peaks in buddlenol A.

The UV spectrum showed no peak above 300 nm implying the absence of a conjugated aromatic–propenal system. Similarly there was no aldehydic proton signal in the ^{1}H NMR spectrum. Decoupling experiments showed that the 1H doublet at δ6.56, the 1H double triplet at δ6.25 and the 2H doublet at δ4.31 were linked and can be assigned to a $-CH{=}CH-CH_2OH$ system. In all other respects the ^{1}H NMR spectrum was identical to that of **4**.



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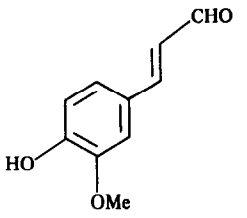
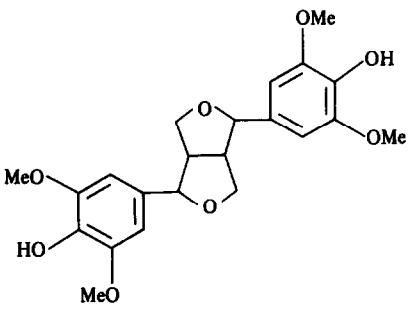


1



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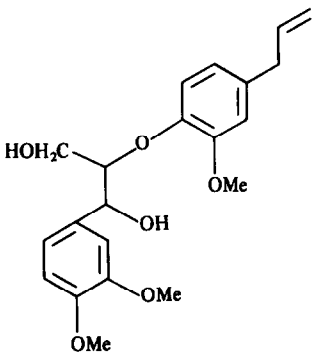

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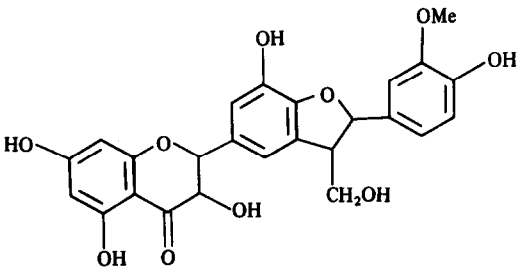


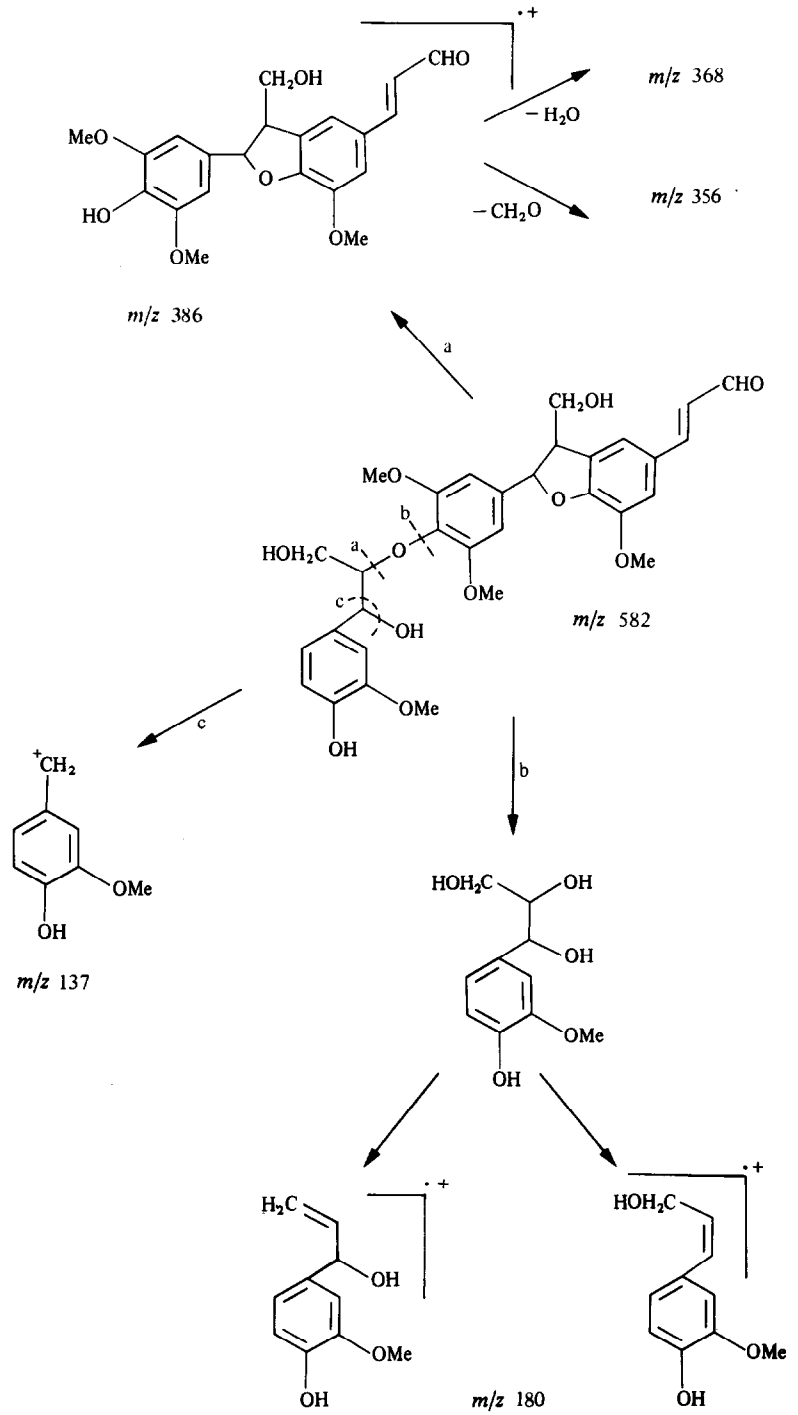
11

The ^{1}H NMR spectrum of the acetate of buddlenol B showed four aliphatic acetates as opposed to three in **4**. An extra $-CH_2OH$ group must therefore be present. Lithium aluminium hydride reduction of buddlenol B afforded a compound whose chromatographic and spectral properties were identical with those of buddlenol A.

It therefore seems probable that buddlenol B is the alcohol corresponding to the aldehyde buddlenol **4** and can be assigned the structure **5**.

Buddlenol C (**6**)

The UV spectrum showed the absence of any conjugated system other than a substituted phenol. The mass spectrum showed a small $[M]^+$ peak at *m/z* 614 and small peaks at *m/z* 566 and 444. The major peaks are at *m/z* 418, 181, 180, 167, 151 and 137. The peaks at *m/z* 137 and 151 are likely to arise from a coniferyl residue and those at *m/z* 167 and 181 from a syringyl (4-OH 3,5-di-OMe phenyl)



Scheme 1. Mass spectral fragmentation of buddlenol A.

residue attached to the alicyclic part of a lignan [11]. Accurate measurement of the *m/z* 180 peak showed that it could be due to coniferyl alcohol ($C_{10}H_{12}O_3$). No such peak at *m/z* 210 was observed for the syringyl residue. Accurate mass measurement showed that the peak at *m/z* 418 had a likely composition of $C_{22}H_{26}O_8$, which is the same as furofurans such as syringaresinol (**3**).

The ^{1}H NMR spectrum shows a signal at δ5.0 which is identical to that observed in buddlenols A and B. The acetylated compound showed the same pair of doublets at *ca* δ6.0 and so this signal can be attributed to the CH adjacent to the aromatic ring of an aryl glycerol which has been isolated as a mixture of *threo* and *erythro* isomers. There is no signal present at *ca* δ5.6 and so it seems that no dihydrobenzofuran ring is present. The 2H finely split doublet at δ4.78, the 2H multiplet at δ4.34, the 2H

multiplet at δ3.12 and a 2H multiplet hidden under the methoxyl peaks at *ca* δ3.9 (but visible in the acetate at δ3.92 having been shifted downfield) are due to the protons of the furofuran ring in such compounds as syringaresinol (**3**). The ^{13}C NMR spectrum (see Table 2) shows signals at δ54.5, 72.1, 85.0 and 87.1 which are typical of the furofuran carbons in lignans with 2,6-diequatorial, diaryl substitution with different aryl groups [14]. It also shows the signals at δ72.8 and 89.2 typical of the C atoms of the aryl glycerol. It therefore seems likely that buddlenol C consists of a furofuran ring with aromatic attachments, one of which has a coniferylglycerol residue attached to it via an ether bridge. Upon EI mass spectrometry, cleavage occurs most easily at this ether bridge to yield the *m/z* 418 peak consisting of the diarylfurofuran. Both the ^{1}H NMR and the ^{13}C NMR spectra showed peaks which were very similar to those given by syringaresinol and so it seems reasonable that this comprises the diarylfurofuran part of the molecule. The linkage is presumably through one of the phenolic hydroxyl groups since the signal at δ5.72 integrates for 2H only and one of these is likely to be the coniferyl hydroxyl. In addition, the mass spectrum of the acetylated compound shows a prominent peak at *m/z* 460 and none at *m/z* 502, thus indicating that only one acetate residue is present in the ion equivalent to *m/z* 418 in the parent compound. The other product arising from the cleavage of the ether bridge loses water and oxygen to give the *m/z* 180 ion. The small peaks at *m/z* 566 and 444 are analogous to fragments seen in the mass spectrum of carinatidiol (**10**) which consist of part of the terminal alcohol of the glycerol, the ether bridge and the non-glycerol part of the molecule [12]. The suggested mass spectral fragmentation is shown in Scheme 2.

In the light of the above evidence it seems that buddlenol C has the structure **6**.

Table 2. ^{13}C NMR data of buddlenol C (20 MHz, $CDCl_3$, TMS as internal standard)

C	Observed	Calculated	Syringaresinol
1	54.5	54.4	54.4
2	85.9	86.0	86.0
4	72.1	71.7	71.8
5	54.5	54.4	54.4
6	87.1	86.2	86.0
8	72.1	71.7	71.8
1′	131.6	132.1	132.0
2′	103.3	102.9	102.9
3′	153.6	153.6	152.9
4′	134.8	134.5	134.5
5′	153.6	153.6	152.9
6′	103.3	102.9	102.9
1″	132.1	132.1	
2″	103.3	102.9	
3″	153.6	153.6	
4″	137.7	136.1	
5″	153.6	153.6	
6″	103.3	103.3	
1‴	131.6	129.1	
2‴	108.8	108.6	
3‴	146.7	146.5	
4‴	145.1	145.6	
5‴	114.3	114.3	
6‴	118.9	119.1	
7‴	72.8	73.9	
8‴	89.2	89.7	
9‴	60.7	61.0	
OMe	56.4	56.0	

Assignments were made with the aid of the DEPT spectra for each compound.

Buddlenol D (**7**)

The $[M]^+$ of buddlenol D is at *m/z* 644 and a more prominent ion is seen at *m/z* 596, both of which are 30 amu more than the corresponding ions in buddlenol C. There are many spectral similarities between the two compounds which indicate that they share the same type of structure, i.e. a furofuran with two aromatic substituents, one of which is attached to an arylglycerol.

Differences are seen in the mass spectrum where the *m/z* peaks 210, 181 and 167 are very prominent whilst those of *m/z* 180, 151 and 137 are much less prominent than in **5**. The increase of 30 amu in both the $[M]^+$ and the prominent ions is due to an extra methoxyl group in the molecule since the signals observed at around δ3.96 integrate for 18H in the ^{1}H NMR spectrum while they integrate for only 15H in the spectrum of buddlenol C (**6**). From the considerations above for the mass spectrum of **5** relating the ions formed to the different parts of the molecule, the high relative abundance of the peaks at *m/z* 210, 181 and 167 make it likely that the extra methoxyl is substituted on the phenylglycerol moiety, i.e. to make a syringyl (4-OH 3,5-diOMe phenyl) glycerol residue. The aromatic proton portion of the ^{1}H NMR spectrum supports this idea since it integrates for 6H rather than 7H.

Buddlenol D is therefore presumed to have the structure 7.

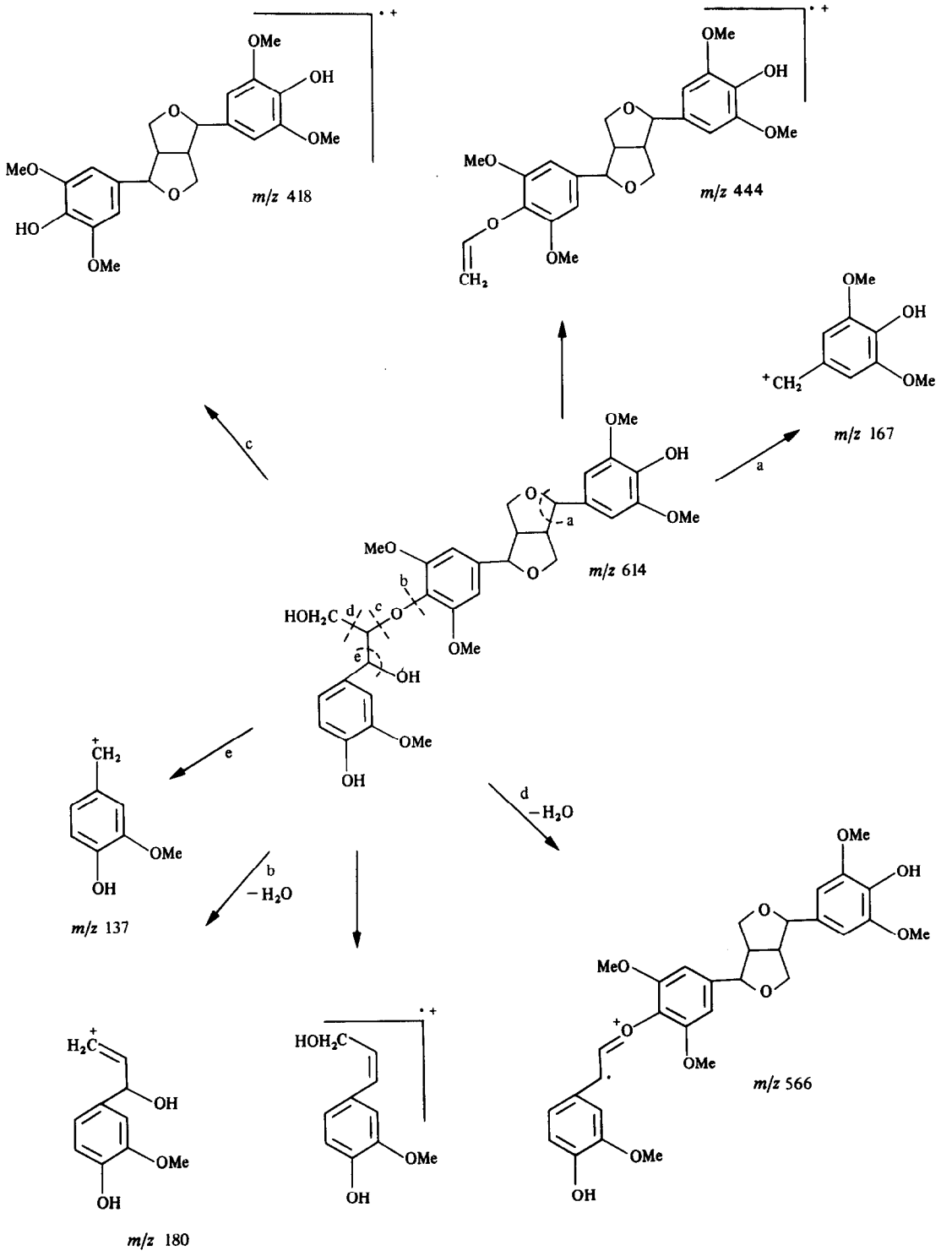
Buddlenol E (**8**)

Buddlenol E shows very similar spectral characteristics to buddlenols C and D and is therefore the same type of compound. The $[M]^+$ is at *m/z* 584, 30 amu less than that for buddlenol C (**6**). Similarly, a peak at *m/z* 536 is seen. Using information from the integration of the methoxyl region of the ^{1}H NMR spectrum and the relatively high relative abundances of the *m/z* peaks at 137, 151 and 180 and the low relative abundances of those at *m/z* 167 and 181 compared with **6**, it is likely that a methoxyl group is absent, probably from the syringyl residue attached directly to the furofuran ring. This substituent would therefore be coniferyl (4-OH 3-OMe phenyl). This would account for the peak at *m/z* 388 as opposed to that at *m/z* 418 in **6** since this peak is due to a fragment incorporating the furofuran ring and its substituents. The 2H singlet seen at δ6.62 in **6** and **7** (due to the *ortho* 2,6 protons) is not observed in **8** because of the more complicated splitting pattern in the 3,4-substituted ring.

Buddlenol E is therefore presumed to have structure **8**.

Buddlenol F (**9**)

The similarity of the spectral data of buddlenol F with that of buddlenols C, D and E shows that it is of the same type of structure. The $[M]^+$ of *m/z* 614 and the peak at *m/z* 566 show that it is isomeric with buddlenol C.



Scheme 2. Mass spectral fragmentation of buddlenol C.

However, there are differences in the mass spectrum with relation to the relative amounts of the ions. The *m/z* 388 peak is very prominent in buddlenol F whereas in buddlenol C the *m/z* 418 peak is much more prominent. As discussed above for buddlenol E, this possibly indicates a coniferyl residue attached directly to the furofuran ring. On the other hand, the peaks of *m/z* 167, 181 and 210 are of greater abundance in the mass spectrum of

9 compared with **6** and this can be attributed to a syringyl rather than a coniferyl glycerol residue being attached to the diaryl furofuran.

Buddlenol F is therefore postulated to have the structure **9**.

General discussion

The compounds isolated are the first lignans to be reported from the Loganiaceae. Buddlenols A–F belong to a novel type of lignan because although some lignans containing aryl glycerol residues have been isolated from the needles of the Pinaceae [13, 15, 16] and neolignans similarly linked from a *Virola* species [12], these are the first reported where the linkage is to a diphenylpropide moiety.

The anisaldehyde spray reagent differentiates between the various types. The dihydrobenzofuran propenals give a yellow colour changing to blue through green whilst the corresponding propenols give a purple colour. The furofuran derivatives give bright pink colours which change to red or red-brown.

The occurrence of buddlenols A (**4**) and B (**5**) is interesting in the light of the traditional use of some *Buddleja* species for treating hepatic disorders since dihydrobenzofuran compounds, e.g. silybin (**11**), exhibit anti-hepatotoxic activity.

The previous reports of alkaloids present in the genus must be viewed with suspicion in the light of the Dragendorff-positive nature of the lignans reported here. An alternative explanation of the positive results obtained might be the formation of artefacts from ammonia used in the screening procedure reacting with other compounds such as the iridoids present.

EXPERIMENTAL

Stems of *B. davidii* were collected from waste ground at Wandsworth Common Station, London SW17, in July 1979. Voucher specimens have been deposited at the herbarium of the Department of Pharmacy, Chelsea College. After being cut into short lengths, the stems were dried, powdered and 500 g of the powder was extracted with hot MeOH by continuous extraction for 5 hr. The MeOH extract was concd under reduced pressure to yield 32 g of a dark red syrup. Dilutions of the syrup gave a positive reaction to Dragendorff's reagent when spotted on paper or silica gel thin layers. Several Dragendorff-positive spots were seen after the mixture was separated by TLC. Very little material was isolated from the MeOH extract by a conventional method for alkaloid extraction and no nitrogen could be detected when a Lassaigne test was performed on the crude MeOH syrup. Consequently alkaloids were assumed to be absent.

25 g of the syrup was dissolved in 500 ml $CHCl_3$–H_2O (1:1). The $CHCl_3$ layer was separated and the H_2O layer extracted with 2 × 100 ml $CHCl_3$ and 2 × 100 ml EtOAc. The organic layers were combined and concd under low pressure to yield 8.9 g brown residue.

8 g residue was dissolved in $CHCl_3$ and fractionated on a silica gel column (50 × 2 cm). The column was eluted with $CHCl_3$ and $CHCl_3$–MeOH mixtures in order of increasing polarity. Fractions of 25 ml each were collected, concd and monitored on TLC. Individual compounds were isolated by prep. TLC (silica gel GF_{254} 1 mm, detected as quenching bands under UV light, 254 nm, eluted with Me_2CO). Crystallization of compounds could not be achieved and their purity was established by their running as single spots in six different TLC systems.

Detection of zones for TLC was by UV (254 nm) when they appeared as quenching areas and by spraying with 0.5% anisaldehyde in HOAc–H_2SO_4–MeOH (2:1:17) and heating at 105° for 10 min. A wide variety of colours was observed which could be classified into three groups according to the colour given, viz. yellow changing through green to blue, purple and pink changing to a deeper, duller red.

Buddlenol A (**4**). 53 mg. On silica gel it gave a yellow colour changing through green to blue on heating after spraying. UV λ_{max}^{MeOH} nm (log ε): 225 (4.91), 276 (3.80) and 334 (4.22); IR ν_{max}^{Nujol} cm^{-1}: 3400 (OH), 1665 (C=O), 1620 (C=C), 1595 (arom. C=C), 1330, 1270, 1215, 1130, 1035, 970; FABMS (glycerol, probe) 70 eV *m/z* (rel. int.): 582 $[M]^+$ (3), 564 (8), 386 (21), 368 (47), 356 (21), 338 (8), 210 (15), 180 (100), 167 (18), 151 (24), 137 (99), 124 (59); ^1H NMR (200 MHz, $CDCl_3$): δ3.61 (2H, *m*, H-9″), 3.85 (3H, *s*, OMe), 3.87 (3H, *s*, OMe), 3.88 (3H, *s*, OMe), 3.95 (3H, *s*, OMe), 4.10 (1H, *m*, H-8″), 5.00 (1H, *d*, H-7″), 5.67 (2H, *m*, H-7′, 4″-OH), 6.5–7.2 (8H, *m*, arom. H, H-8), 7.41 (1H, *d*, *J* = 16 Hz, H-7), 9.64 (1H, *d*, *J* = 8 Hz, H-9); ^{13}C NMR: see Table 1.

Buddlenol A acetate. EIMS (probe) 70 eV *m/z* (rel. int.): 428 (10), 368 (80), 222 (100), 179 (60); ^1H NMR (200 MHz, $CDCl_3$): δ1.99 (3H, *s*, OAc), 2.10 (3H, *s*, OAc), 2.14 (3H, *s*, OAc), 2.29 (3H, *s*, arom. OAc), 3.72 (3H, *s*, OMe), 3.80 (3H, *s*, OMe), 3.81 (3H, *s*, OMe), 3.95 (3H, *s*, OMe), 4.2–4.7 (4H, *m*, H-8′, H-8″, H-9″), 5.52 (1H, *d*, *J* = 6.7, H-7′), 6.12 (1H, overlapping *ds*, *J* = 6.2, H-7‴), 6.5–7.2 (8H, *m*, H-8, arom. H), 7.42 (1H, *d*, *J* = 18.0 Hz, H-7), 9.67 (1H, *d*, *J* = 8.0 Hz, H-9).

Buddlenol B (**5**). 46 mg. On silica gel it gave a purple colour on heating after spraying. UV λ_{max}^{MeOH} nm (log ε): 227 sh (4.7), 274 (3.2); IR ν_{max}^{Nujol} cm^{-1}: 3400 (OH), 1620 (C=C), 1590 (arom. C=C), 1320, 1280, 1220, 1130, 1035; FABMS (glycerol, probe) 70 eV *m/z* (rel. int.): 584 $[M]^+$ (3), 566 (3), 388 (23), 370 (42), 358 (16), 340 (12), 339 (18), 180 (100), 151 (11), 137 (59), 124 (42); ^1H NMR (200 MHz, $CDCl_3$): δ3.61 (2H, *m*, H-9″), 3.84 (3H, *s*, OMe), 3.87 (3H, *s*, OMe), 3.89 (3H, *s*, OMe), 3.95 (3H, *s*, OMe), 4.10 (1H, *m*, H-8″), 4.31 (2H, *d*, *J* = 5.9 Hz, H-9), 5.00 (1H, *m*, H-7″), 5.62 (2H, *m*, H-7′, *J* = 6.7 Hz, 4″-OH), 6.25 (1H, *dt*, *J* = 14, *J* = 5.9 Hz, H-8), 6.56 (1H, *d*, *J* = 14 Hz, H-7), 6.6–7.0 (7H, *m*, arom. CH); ^{13}C NMR: see Table 1.

Buddlenol B acetate. EIMS (probe) 70 eV *m/z* (rel. int.): 514 (51), 472 (12), 470 (16), 454 (170), 412 (57), 352 (65), 323 (48), 281 (12), 222 (100), 179 (42), 162 (51); ^1H NMR (200 MHz, $CDCl_3$): δ1.97 (3H, *s*, OAc), 2.05 (3H, *s*, OAc), 2.11 (3H, *s*, OAc), 2.14 (3H, *s*, OAc), 2.30 (3H, *s*, arom. OAc), 3.72 (3H, *s*, OMe), 3.74 (3H, *s*, OMe), 3.82 (3H, *s*, OMe), 3.92 (3H, *s*, OMe), 4.2–4.6 (6H, *m*, H-8′, H-8″, H-9′, H-9″), 4.71 (2H, *d*, *J* = 6.7 Hz, H-9), 5.45 (1H, *d*, *J* = 7.2 Hz, H-7′), 6.15 (2H, *m*, H-7″, H-8), 6.6–7.0 (8H, *m*, H-7, arom. H); ^{13}C NMR: see Table 1.

Buddlenol C (**6**). 230 mg. On silica gel after spraying and heating it gave a greenish-pink colour changing to brown-red. UV λ_{max}^{MeOH} nm (log ε): 226 sh (3.1), 276 (1.2); IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 1605 (arom. C=C), 1530, 1520, 1280, 1230, 1125, 1040; EIMS (probe) 18 eV *m/z* (rel. int.): 614 $[M]^+$ (1), 566 (4), 444 (5), 418 (50), 210 (10), 181 (20), 180 (100), 167 (10), 151 (50), 137 (90); Found: *m/z* 566.2101; $C_{31}H_{34}O_{10}$ requires: 566.2141; found: *m/z* 418.1627; $C_{22}H_{26}O_8$ requires: 418.1627; found: 180.0780; $C_{10}H_{12}O_3$ requires: 180.0786. ^1H NMR (200 Mz, $CDCl_3$): δ3.12 (2H, *m*, H-1, 5), 3.2–3.6 (2H, *m*, H-9″), 3.87 (6H, *s*, 2 × OMe), 3.90 (6H, *s*, 2 × OMe), 3.93 (3H, *s*, OMe), 3.8–4.0 (2H, *m*, H-4, H-8), 4.15 (1H, *m*, H-8‴), 4.34 (2H, *m*, H-4, H-8), 4.78 (2H, *d*, *J* = 5.0 Hz, H-2, H-6), 5.0 (1H, *s* (*br*), H-7‴), 5.72 (2H, *s* (*br*), disappears on deuteration, HO-4′, HO-4‴), 6.6–7.0 (5H, *m*, arom. H); ^{13}C NMR: see Table 2.

Buddlenol C acetate. EIMS (probe) 18 eV *m/z* (rel. int.): 460 (20), 418 (5), 222 (100), 180 (20), 179 (30), 162 (45); ^1H NMR:

δ1.98 (3H, *s*, 9″-OAc), 1.99 (3H, *s*, 7″-OAc), 2.16 (3H, *s*, 4′-OAc), 2.35 (3H, *s*, 4″-OAc), 3.12 (2H, *m*, H-1, H-5), 3.2–3.6 (1H, *m*, H-9″), 3.74 (6H, *s*, 2 × OMe), 3.78 (6H, *s*, 2 × OMe), 3.82 (3H, *s*, OMe), 3.92 (2H, *m*, H-4, H-8), 4.20–4.78 (5H, *m*, H-4, H-8, H-8″, H-2, H-6), 6.12 (1H, *m*, H-7″), 6.62 (2H, *s*, arom. H), 6.65–7.0 (5H, *m*, arom. H).

Buddlenol D (**7**). 67 mg. On silica gel after spraying and heating it gave a bright pink colour. UV λ_{max}^{MeOH} nm (log ε): 238 sh (3.8), 275 (2.4), 280 sh (2.3); IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 1605 (arom. C=C), 1530, 1520, 1280, 1230, 1125, 1040; EIMS (probe) 18 eV *m/z* (rel. int.): 644 [M]$^+$ (3), 596 (5), 472 (10), 418 (80), 226 (18), 210 (91), 193 (47), 182 (33), 181 (65), 180 (27), 167 (78), 154 (33), 137 (14); ^{1}H NMR (200 Mz, $CDCl_3$): δ3.12 (2H, *m*, H-1, H-5), 3.2–3.6 (2H, *m*, H-9‴), 3.92 (3H, *s*, OMe), 3.96 (12H, *s*, 4 × OMe), 3.97 (3H, *s*, OMe), 3.8–4.0 (2H, *m*, H-4, H-8), 4.12 (1H, *m*, H-8‴), 4.34 (2H, *m*, H-4, H-8), 4.78 (2H, *d*, *J* = 5.0 Hz, H-2, H-6), 5.0 (1H, *s* (*br*), H-7‴), 5.56 (2H, *s* (*br*), disappears on deuteration, HO-4′, HO-4‴), 6.62 (2H, *s*, arom. H), 6.65–7.0 (4H, *m*, arom. H).

Buddlenol E (**8**). 42 mg. On silica gel after spraying and heating it gave a bright pink colour. UV λ_{max}^{MeOH} nm (log ε): 232 sh (2.8), 266 (3.3); IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 1610 (arom. C=C), 1535, 1520, 1270, 1210, 1135, 1050; EIMS (probe) 18 eV *m/z* (rel. int.): 584 [M]$^+$ (3), 536 (15), 442 (5), 388 (100), 180 (65), 167 (20), 151 (60), 137 (80), 124 (40); ^{1}H NMR (200 Mz, $CDCl_3$): δ3.11 (2H, *m*, H-1, H-5), 3.2–3.6 (2H, *m*, H-9‴), 3.86 (3H, *s*, OMe), 3.90 (6H, *s*, 2 × OMe), 3.96 (3H, *s*, OMe), 3.8–4.0 (2H, *m*, H-4, H-8), 4.12 (1H, *m*, H-8‴), 4.34 (2H, *m*, H-4, H-8), 4.78 (2H, *d*, *J* = 5.0 Hz, H-2, H-6), 5.0 (1H, *s* (*br*), H-7‴), 5.56 (2H, *s* (*br*), disappears on deuteration, HO-4′, HO-4‴), 6.5–6.9 (8H, *m*, arom. H).

Buddlenol F (**9**). 38 mg. On silica gel after spraying and heating it gave a bright pink colour changing to red. UV λ_{max}^{MeOH} nm (log ε): 226 sh (3.8), 275 (2.2); IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 1605 (arom. C=C), 1530, 1520, 1280, 1230, 1125, 1040; EIMS (probe) 18 eV *m/z* (rel. int.): 614 [M]$^+$ (1), 566 (3), 418 (30), 388 (55), 210 (10), 193 (17), 182 (40), 181 (100), 180 (60), 167 (80), 151 (30), 137 (65); ^{1}H NMR (200 MHz, $CDCl_3$): δ3.12 (2H, *m*, H-1, H-5), 3.2–3.6 (2H, *m*, H-9‴), 3.86 (3H, *s*, OMe), 3.90 (12H, *s*, 4 × OMe), 3.8–4.0 (2H, *m*, H-4, H-8), 4.15 (1H, *m*, H-8‴), 4.34 (2H, *m*, H-4, H-8), 4.78 (2H, *d*, *J* = 5.0, H-2, H-6), 5.0 (1H, *s* (*br*), H-7‴), 5.72 (2H, *s* (*br*), disappears on deuteration, HO-4′, HO-4‴), 6.5–7.0 (7H, *m*, arom. H).

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