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REVISED STRUCTURES FOR PLUVIATILOL, METHYL PLUVIATILOL AND XANTHOXYLOL

GENERAL METHODS FOR THE ASSIGNMENT OF STEREOCHEMISTRY TO 2,6-DIARYL-3,7-DIOXABICYCLO[3.3.0]OCTANE LIGNANS

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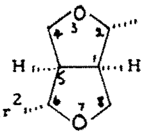
Abstract—The isolation and characterisation of methyl piperitol, (+)-epieudesmin and (+)-episesamin from the stem bark of *Zanthoxylum acanthapodium* is reported. The ^1H and ^{13}C NMR spectra are correlated with those of other known lignans and it is shown that ^{13}C NMR shifts can be used to assign unambiguously the nature and configuration of the aryl groups in unsymmetrically substituted 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octanes. Other less satisfactory methods which have in the past been used for this purpose are discussed and in particular the use of coupling constants to assign stereochemistry in this series is strongly criticised. Revised structures for pluviatilol, methyl pluviatilol (fargesin) and xanthoxylol are proposed.

Recently one of us (E.V.R.) reported the isolation of (±)-eudesmin **1a**, (+)-sesamin **1b**, and fargesin from the stem bark of the medicinal plant *Zanthoxylum acanthapodium* D.C.[1] Further examination gave three other lignans, two of which were identified by mass spectrometry[2] and NMR[3] as (+)-epieudesmin **2a**[4] and (+)-episesamin **2b**.[5] The third compound was identified as almost racemic methyl piperitol (**1c** ≡ **1d**), $[\alpha]_D + 13°$, previously isolated as desmethoxyaschantin, $[\alpha]_D + 73.6°$, by Hänsel.[6] The detailed ^1H NMR spectrum of this compound has not been published, and is compared in Table 1 with the spectra of the closely related (−)-ethyl piperitol and (−)-piperitol (**1e** ≡ **1f**).[7]† The mass spectrum of methyl piperitol had the expected dual breakdown, the peaks being identified as shown (Fig. 1).



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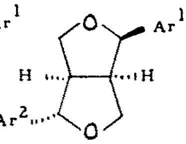

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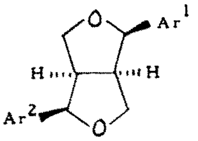

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(**a**) $Ar^1 = Ar^2$ = veratryl
(**b**) $Ar^1 = Ar^2$ = piperonyl
(**c**) Ar^1 = veratryl, Ar^2 = piperonyl
(**d**) Ar^1 = piperonyl, Ar^2 = veratryl
(**e**) Ar^1 = guaiacyl, Ar^2 = piperonyl
(**f**) Ar^1 = piperonyl, Ar^2 = guaiacyl
(**g**) $Ar^1 = Ar^2$ = 3,4,5-trimethoxyphenyl
(**h**) $Ar^1 = Ar^2$ = syringyl
(**i**) Ar^2 = piperonyl, Ar^1 = 3,4,5-trimethoxyphenyl
(**j**) Ar^2 = veratryl, Ar^1 = 3,4,5-trimethoxyphenyl.

The fact that all the methylene protons come below

Table 1.*

	Piperitol ethyl ether[7]	Piperitol methyl ether	Piperitol[7]
H2/6	5.28d (4.0)	5.29d (3)	5.28d (4.5)
H1/5	6.75 - 7.10m	6.92m	6.75 - 7.15m
H4a/8a	6.14dd (9.0, 3.7)	6.15m	6.15dd (9.0, 3.5)
H4e/8e	5.74dd (9.0, 7.5)	5.76dd (9, 6)	5.74dd (9.0, 6.5)
OMe	6.11s	6.13s, 6.16s	6.10s
OCH_2O	4.06s	4.10s	4.04s
arom.	3.06 - 3.25m	3.1 - 3.3m	2.07 - 3.24m

* Chemical shifts in τ, coupling constants in Hz in parentheses.
All spectra run in $CDCl_3$.
Signals due to OEt and OH groups are not included.

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†In fact the formulae shown represent the absolute configuration of the (+)-series, the (−)-series being the mirror images of the structures shown.

τ6.3, together with the near equivalence of the corresponding aliphatic protons, showed that the compound was highly symmetrical and diequatorial. Thus it had to be almost racemic methyl piperitol **1c** ≡ **1d**. As expected, reaction with ethanolic hydrogen chloride yielded some fargesin.

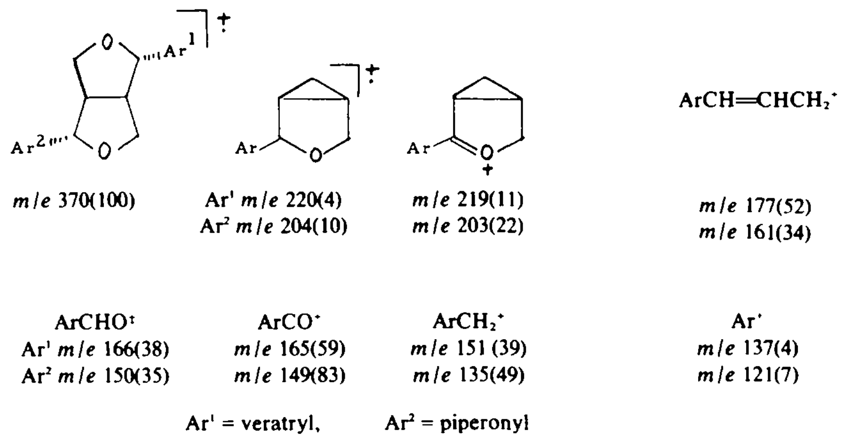
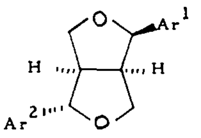


Fig. 1.

The isolation of fargesin[8] and its production from methyl piperitol caused us to reconsider its structure. Careful comparison of the IR spectra of fargesin with those of methyl pluviatilol[9] and methyl xanthoxylol[7] (previously assigned structures **2f** and **2e** respectively, but see later) showed that fargesin was almost racemic methyl pluviatilol.† However on retracing the "proofs" of the structures of pluviatilol and xanthoxylol we were struck by the tenuousness of the arguments used. We therefore re-examined the methods which had been used to determine the structures of all known epi-isomers of lignans bearing two different aryl groups, and concluded that in no case was there a satisfactory proof of structure.

In general by a combination of ¹H NMR,[3] mass spectrometry[2] and optical methods,[5] the structures of symmetrically substituted 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octanes can be rapidly established. Even when the two aryl groups are different, so long as they are both equatorial or both axial the problem is readily solved, as above for methyl piperitol. However, when both aryl groups are different and the compound belongs to the epi-series, then the question of deciding between the two alternatives 2 and 4 is considerably more difficult. This is particularly so as both aryl groups are generally substituted with alkoxy groups and are very similar in nature. Up to now the methodology used has, as we will show, led to errors in structural assignment.



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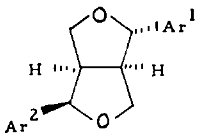

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Mass spectrometry will not differentiate between stereoisomers[2] and therefore the question has been tackled by means of ¹H NMR spectroscopy. The problem can be divided into two parts: (i) to decide which benzylic proton is axial and which is equatorial, and (ii) to decide which aryl group is associated with each benzylic hydrogen atom.

With regard to the first part of this problem, two methods have been used to assign the stereochemistry of the benzylic protons. One is based on early work by Ludwig *et al.*[10] who compared the τ values and coupling constants of the benzylic protons of pinoresinol (τ5.28 d, J4.6) and epipinoresinol (τ5.14d, J5.0; τ5.56d, J7.0). They argued that the low field proton in epipinoresinol was axial, as was the corresponding proton in pinoresinol, and assumed that it obeyed the Karplus equation. However these workers did not have a sample of diapinoresinol to complete the comparison. Becker and Beroza[11] compared all three isomers **1b**, **2b** and **3b** in the sesamin series, whilst Pelter *et al.*[3] did the same for the eudesmin series **1a**, **2a** and **3a**. A further series of comparisons involving yangambin **1g**, lirioresinol A **2h**, and diayangambin **3g** has also appeared.[12] The values found for the benzylic protons in these compounds are shown in Table 2.

Quite consistently the diequatorial and diaxial series are more akin to each other than either is to the epi-series and obviously assignment of stereochemistry to the benzylic protons of the epi-compounds cannot be made by simple comparison. Moreover the coupling constants in the diequatorial and diaxial series are so similar that they are clearly not indicative of stereochemistry. Both Beroza and Pelter stressed this point and backed it by the ¹H NMR spectra of various derivatives. The epi-series is anomalous in showing one of the benzylic protons at high field, and this feature is shared by all the known epi-compounds. We suggest that this is an important and diagnostic characteristic of the epi-compounds and that like the 8-axial protons (see below) it is a result of a direct anisotropic field effect of an axial aryl group in the 2-position. This analysis is supported by the fact that the epi-series is the only one in which a benzylic proton is held close to an axial aryl group in the opposite ring as in **5**. In the diequatorial series both of the aryl groups are of course equatorial while in the diaxial series there are no axial benzylic protons to be influenced. This indicates that in the epi-compounds the high field proton is the axial proton and this directly solves the problem of assigning the stereochemistry at C-2 and C-6. However, this assignment is the opposite of that made by Ludwig *et al.*

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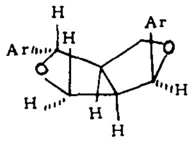
†We thank Profs. Ritchie and Okabe for kindly supplying us with copies of the spectra of methyl pluviatilol and methyl xanthoxylol.



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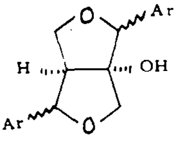

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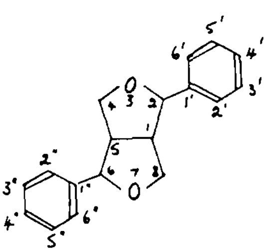

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Table 2. τ Values of benzylic protons of 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octanes

Compound	1a	2a	3a	1b	2b	3b	1g	2h	3g
τ	5.25	5.55, 5.15	5.10	5.33	5.64, 5.24	5.14	5.25	5.59, 5.17	5.02
J	4	7 5.5	5	4.6	6.7 5.0	5.1	4	7.5 5	5

Table 3. Positions of benzylic protons in gmelinols

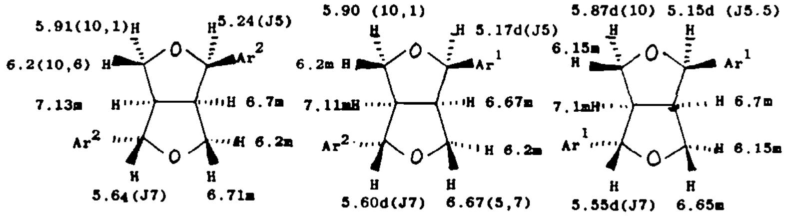
	Gmelinol	Isogmelinol	Neogmelinol
H-6	(eq.) 4.81d (J 6)	(ax.) 5.15d (J 5)	(ax.) 5.52d (J 8)
H-2	(ax.) 5.43s	(ax.) 5.17s	(eq.) 5.28s

It should be noted that Pelter *et al.*[13] in their study of the gmelinols gave the assignments in Table 3 to the benzylic protons at C-2 and C-6 which are readily distinguished as one is a singlet and the other a doublet (Table 3).

The equatorial/axial assignments for these compounds were made by another method (see later) but are in complete agreement with the present analysis. Once more, as was stated, the coupling constants are not indicative of stereochemistry. A similar situation was found for paulownin and isopaulownin.[14]

Despite all this, coupling constants continue to be used to assign stereochemistry to these lignans, and for example, Haslam[15] assigned the stereochemistry of sesangolin on this basis. More pertinently, having found that the proton at τ5.17 (J 5.2) rather than the proton at τ5.58 (J 6.6) was associated with the guaiacyl ring in pluviatilol (see below), Ritchie *et al.*[9] stated that on the basis of the coupling constant this must be an axial proton and so the phenolic ring must be equatorial and the piperonyl ring axial. Hence pluviatilol was assigned structure **2f**[9] and xanthoxylol **2e**.[7] Methyl pluviatilol (fargesin) would then be **2d**. Similarly Nishino[16] assigned structures to epiaschantin and epimagnolin on the same basis (see later).

The second method for assignment of stereochemistry was proposed by Pelter *et al.*[3,13] and was based upon an examination of models. These show that an axial aryl group is held very close indeed to the axial proton of the methylene group of the opposite ring, i.e. an axial C-2 aryl group would affect H-8 (axial) and an axial C-6 aryl group would affect H-4 (axial). The result anticipated would be an upfield shift of the axial proton. The method was tested upon the complete eudesmin series, the sesamins and the gmelinols. It has since been applied to many compounds including the yangambins,[12] the excelsins,[17] the aschantins,[18] and the arboreols.[19] In eudesmin there are two methylene protons between τ5.6 and 5.8 and two between τ6.0 and 6.2. In diaeudesmin no methylene protons appear below τ6.0 and two appear above τ6.35, whilst epieudesmin has one proton between τ5.6 and 5.9, two at τ6.2–6.3 and the other at τ6.55–6.75. This clear-cut distinction is also seen for the gmelinols, yangambins, etc. and appears to provide a general method for assigning stereochemistry. It can be extended, by decoupling the two ABXY systems present, and hence the equatorial benzylic proton associated with the high field methylene proton can be unequivocally established. *In every case the high field benzylic proton is axial*, in agreement with our previous analysis.



Episesamin Methyl Pluviatilol Epieudesmin†

Ar^2 = piperonyl, Ar^1 = veratryl

Fig. 2.

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†These assignments correct an inadvertent error in the previous assignments for epieudesmin.[3] Examination of the original spectra, as well as decouplings, by the authors support the present assignments.

Turning now to the second part of the general problem outlined earlier, two methods have been used to decide which aryl group is adjacent to each benzylic proton. When there is a free 4′-hydroxyl group as in pluviatilol and xanthoxylol, the production of the anion,[9] or acetylation,[7] causes a shift of the signal due to the adjacent benzylic proton. This was verified on various model substances and by its use the proton at τ5.17 (J 5.2) in pluviatilol was shown to be adjacent to the guaiacyl ring,[9] whilst in xanthoxylol the high field proton at τ5.60 (J 6.7) was so placed.[7] In our opinion this method is completely reliable, and together with our assignment of stereochemistry to the highfield benzylic proton as axial, means that pluviatilol must be formulated as **2e** and xanthoxylol as **2f**. This reverses the previous assignments based on an incorrect identification of the axial and equatorial protons. Furthermore, if it is accepted that the protons in pluviatilol methyl ether at τ5.17 d (J 4.5) and τ5.60 d (J 6.6) correspond to the benzylic protons at τ5.17 d (J 5.2) and τ5.58 d (J 6.6) in pluviatilol, then the structure of methyl pluviatilol (fargesin) is **2c** and not **2d** as previously proposed. Unfortunately, this method of associating benzylic protons and aryl groups is confined to those compounds having one free appositely placed phenolic group and to compounds directly derived from them.

A more general approach was suggested by Nishino and Mitsui[16] who studied the effect of a europium shift reagent on the benzylic, methoxyl, methylenedioxy, and aromatic protons of epiaschantin (**2i**) and epimagnolin (**2j**). They assumed that the ring giving the greatest shifts for both the substituent groups and aromatic protons would be associated with the benzylic proton undergoing the larger shift. It seemed to us that this method was open to question *a priori* since it made the assumption that the major effect upon the benzylic proton was due to complexation at a remote position on the substituted benzene ring. It ignored the probability that the aliphatic ring oxygen adjacent to the benzylic position would complex with the shift reagent and that differential shifts would thus be obtained on the basis of differing stereochemistry at the benzylic positions.

This proposition was very simply tested by examining the behaviour of episesamin **2b** and aschantin **1i** with a shift reagent. According to the reasoning of the Japanese workers, as the aryl groups in episesamin are the same, the shifts of the benzylic protons should be the same. In fact at a ratio of 1:4 of Eu(fod)$_3$ to episesamin (in CDCl$_3$, 0.3 ml) the axial proton moved downfield by 50 Hz and the equatorial one by 21 Hz. The methylenedioxy protons hardly moved (<1 Hz). Further additions of the shift reagent showed that the shifts were linear. Hence it is clear that differential shifts are not wholly a function of different aryl groups but are also a function of the stereochemistry at C-2 and C-6. That the aryl groups *do* indeed make a difference was shown by repeating the same experiment with aschantin in which both of the benzylic protons are axial but the aryl groups differ. Here the shifts of the two benzylic protons were 24 Hz and 33 Hz. The actual shifts obtained for unsymmetrical compounds of the epi-series such as **2c** must therefore depend upon a delicate balance between stereochemical factors and the associated aryl group.

If however we were to assume that Nishimo *et al.* had succeeded by the use of shift reagents in correctly associating the two different aryl groups with specific benzyl protons, then their assignments of the stereochemistry in epiaschantin and epimagnolin must still be reversed since they incorrectly assigned the proton at τ5.16 d (J5) to an axial proton and that at τ5.57 d (J7) to an equatorial proton. However, as the europium shift method is not reliable in this context, these structures must be left open for the present.

Despite the fact that the use of ^{1}H NMR spectra had led

Table 4. ^{13}C NMR spectra of 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octanes*

Carbon	Eudesmin	Sesamin	Yangambin	Aschantin	Methyl Piperitol	Epieudesmin	Episesamin	Methyl Pluviatilol	Diaeudesmin
5	54.31	54.24	54.37	54.26	54.07	54.44	54.76	54.52	49.49
1				54.38	54.26	50.11	50.26	50.03	
4	71.72	71.55	71.96	71.67	71.61	70.92	71.04	70.84	68.75
8				71.90		69.64	69.70	69.58	
6	85.77	85.61	85.91	85.69	85.61	87.53	87.71	87.48	83.96
2				85.92	85.66	81.96	82.11	81.82	
1″	134.04	134.93	136.64	134.93	134.94	133.51	135.63	135.08	131.38
1′				136.67	133.38	130.81	132.65	130.86	
			137.48	137.44	146.87	147.83	146.84	146.93	
3′3″	148.85	146.86	(4′)	146.44	147.74	148.54	147.44	147.72	147.98
4′4″	149.46	147.74		147.85	148.43	148.67	147.94	147.82	148.69
			153.33	153.30	148.99	149.05	148.24	148.66	
			(3′5′)	102.82	106.33	108.87	106.61	106.33	
2′2″	109.67	106.32	102.84	106.38	107.99	109.01	106.71	107.91	109.58
5′5″	111.45	107.96	(2′6′)	108.08	109.10	110.91(x2)	108.26	108.93	110.93
				119.21	110.93			110.97	
6′6″	118.36	119.13			118.07	117.58	118.89	117.56	118.36
					119.15	118.32	119.65	119.28	
OMe	55.57	-	56.20	56.15	55.84	55.85		55.77	55.84
	55.90		60.81	60.79					
OCH$_2$O	-	100.89	-	100.99	100.90	-	101.14	100.86	-

*All values given as p.p.m. downfield from TMS. All spectra nm in CDCl$_3$.

to a reversal of the structures of pluviatilol and xanthoxylol, the assignments depended upon the special situation in which an aryl group with a 4′-phenolic group is associated with a particular benzylic proton. A general solution to the problem did not seem to be at hand using ^{1}H NMR and we therefore turned our attention to the ^{13}C NMR spectra. In particular we wondered whether the 1′ and 1″ positions of the aromatic rings (see 7 for numbering) might be sensitive both to the substituents on the aromatic ring and also to the stereochemistry at the neighbouring benzylic position. Some ^{13}C NMR spectra of lignans are shown in Table 4, all assignments being supported by off-resonance spectra. In Table 5 the relevant data for the 1′ and 1″ positions are abstracted. The compounds starred (*) are either diequatorial or diaxial so their assignments are unequivocal. Clearly the 1′, 1″ carbon atoms of equatorial and axial veratryl groups are distinct from each other and from piperonyl groups in similar positions. They are also distinguished from equatorial 3,4,5-trimethoxyphenyl groups. The assignment of the 1′ and 1″ carbon atoms of epieudesmin **2a** follows, as from similar considerations does the assignment of the 1′ and 1″ carbon atoms of episesamin. Any reversal of these assignments would lead to glaring anomalies. Furthermore the spectrum of methyl pluviatilol in which the benzylic carbon atoms are separated by >4 ppm can only be interpreted as shown and this provides completely independent confirmation that veratryl group must be axial and the piperonyl group equatorial in this compound.

The method of using the signals corresponding to the 1′,1″ carbon atoms seems to be reasonably general, in

Table 5. Position of 1′ and 1″ carbon atoms of 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octanes

Equatorial veratryl group		Axial veratryl group	
*Eudesmin	134.04	*Diaeudesmin	131.38
*Methyl piperitol	133.38	Epieudesmin	130.81
Epieudesmin	133.51	Methyl pluviatilol	130.86
Equatorial piperonyl group		**Axial piperonyl group**	
*Sesamin	134.93	Episesamin	132.65
*Aschantin	134.93		
*Methyl piperitol	134.94		
Episesamin	135.63	**Equatorial 3,4,5-trimethoxy phenyl group**	
Methyl pluviatilol	135.08	*Aschantin	136.67
		*Yangambin	136.64

Table 6. ^{13}C NMR values of aliphatic carbon atoms of 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octane lignans

	2/6	1/5	4/8
Equatorial aryl			
*Eudesmin	85.77	54.31	71.72
*Sesamin	85.61	54.24	71.55
*Yangambin	85.91	54.37	71.96
*Methyl piperitol	85.61, 85.66	54.07, 54.26	71.61
*Aschantin	85.69, 85.92	54.26, 54.38	71.67, 71.90
Epieudesmin	87.53	54.44	70.92
Episesamin	87.71	54.76	71.04
Methyl pluviatilol	87.48 ↑ Decoupled specifically by irradiation at 440 Hz downfield from TMS	54.52[a]	70.84
Axial aryl			
*Diaeudesmin	83.96	49.49	68.75
Epieudesmin	81.96	50.11	69.64
Episesamin	82.11	50.26	69.70
Methyl pluviatilol	81.82 ↑ Decoupled specifically by irradiation at 483 Hz downfield from TMS	50.03[a]	69.58

(a) Signal at 54.52 p.p.m. specificially decoupled by irradiation at 289 Hz; signal at 50.03 p.p.m. specifically decoupled by irradiation at 333 Hg.

which case all that is required to solve stereochemical problems in this field is careful inspection of the ^{13}C NMR data. Some caution may however be required in dealing with lignans with a 2'-alkoxy group which could undergo conformational changes, as does lonchocarpan.[20] The structures of epiaschantin and epimagnolin should be readily decided by this method. Further points of interest are seen by examining the 2,6-, 1,5- and 4,8-carbon atoms (Table 6). Clearly these carbon atoms are sensitive to stereochemical changes at C-2 and C-6 but not to changes of the aryl group. They can however be used to confirm our assignments in the ^{1}H NMR spectra by specific irradiation experiments. Thus the benzylic carbon atom bearing an axial aryl group is specifically decoupled by irradiating the low field benzylic proton, and the benzylic carbon atom bearing an equatorial aryl group is specifically decoupled by irradiating the high field proton. This provides independent proof of our proton assignments made on the basis of the anisotropic effect of the aryl group.

EXPERIMENTAL

Mass spectra were obtained using an AEI MS9 double-focussing spectrometer. ^{1}H and ^{13}C NMR spectra were obtained using Varian HA100 and XL100 instruments respectively.

Extraction of stem bark of Z. acanthapodium

The dried stem bark of *Zanthoxylum acanthapodium* DC was coarsely powdered in a Wiley mill. The material (1 kg) was extracted with light petroleum (4 l) in a Soxhlet extractor. The petroleum ether extract on concentration in vacuo gave a brownish residue (34.4 g). The residue became partly crystalline after a week. The crystalline solid was separated from the syrupy residue by dissolving the latter in benzene-petroleum ether and filtering. The filtrate was concentrated *in vacuo* and the residue (10 g) was chromatographed over silica gel (finer than 200 mesh) and eluted with solvents of increasing polarity. The fractions were purified by repeated crystallisations until the compounds were homogeneous by TLC. Six pure lignans were obtained in the order indicated in Table 7.

Identification of (+)-episesamin

The compound (120 mg) crystallised as white needles from acetone-petroleum ether, m.p. 121–2°, $[\alpha]_D + 120°$ (CHCl$_3$) (lit.[5] m.p. 121.5°, $[\alpha]_D + 124°$). Labat test gave a green colour.

Identification of (±)-methyl piperitol

The compound (250 mg) crystallised as white plates from ether-petroleum, m.p. 68–71°, $[\alpha]_D + 13°$ (CHCl$_3$) (lit.[6] m.p. 75°, $[\alpha]_D + 73.6°$). (Found: M$^+$ 370.1422. $C_{21}H_{22}O_6$ requires: 370.1416). Labat test gave a transient green colour.

Identification of (+)-epieudesmin

The compound (100 mg) crystallised as white flakes from benzene-petroleum ether, m.p. 128–9°, $[\alpha]_D + 111°$ (CHCl$_3$) (lit.[5] m.p. 125–6°, $[\alpha]_D + 119°$).

KMnO$_4$ *oxidation of methyl piperitol*

Methyl piperitol (50 mg) was dissolved in methanol (2.5 ml) and KMnO$_4$ (300 mg) dissolved in water (0.5 ml) and acetone (1.5 ml) was added. The mixture was continuously stirred at 45–55° for 30 min. More KMnO$_4$ (50 mg in 1 ml water) was added and the reaction mixture left overnight with stirring at 45–55°. SO$_2$ was bubbled into the cooled solution. It was then extracted with chloroform and the choroform extract washed with water and bicarbonate solutions. The latter was acidified with dilute HCl and extracted with chloroform. The chloroform extract showed two spots by TLC. Comparison with authentic samples of veratric acid and piperonylic acid by TLC using toluene-ethyl formate-formic acid (5:4:1), showed the presence of these two acids. The concentrated chloroform extract gave a crystalline solid. m.p. 178–9°, on standing which was identified as veratric acid (5 mg). The residue obtained from the mother liquor on repeated crystallisation from methanol gave piperonylic acid (3 mg), m.p. 237–9°.

Isomerisation of methyl piperitol to methyl pluviatilol

Methyl piperitol (50 mg) was dissolved in methanol (2.5 ml) and concentrated hydrochloric acid (2–3 drops) was added. The mixture was refluxed for 1 hr on a water bath. The methanolic HCl was removed from the mixture by concentrating it under reduced pressure. On crystallisation from benzene-petroleum ether the reaction mixture yielded methyl pluviatilol (30 mg) which was identified by TLC, m.p and m.m p.

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Table 7. Compounds isolated by column chromatography

Compound	Eluent
(+)-episesamin	benzene-chloroform (98:2)
(+)-sesamin	benzene-chloroform (9:1)
(±)-fargesin	benzene-chloroform (3:1 and 1:1)
(±)-methyl piperitol	chloroform and chloroform-methanol (99:1)
(+)-epieudesmin	chloroform-methanol (95:5)
(±)-eudesmin	chloroform-methanol (9:1)