Isoflavonoid and Pterocarpinoid Extractives of *Lonchocarpus laxiflorus*

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Two new members of the rare isoflavan series and two new pterocarpans have been isolated from *Lonchocarpus laxiflorus*. Physical methods involved in solving the structural problems associated with the penta-substituted ring B of three of these compounds include the study of methoxy-proton shifts and i.r. stretching frequencies. Some possible errors of the method of methoxy-proton shifts are pointed out. Steric factors result in one isoflavan (lonchocarpan) and its derivatives taking up unusual conformations; this gives rise to misleading o.r.d. curves and is also reflected in the n.m.r. spectra.

THE leguminous bush or tree *Lonchocarpus laxiflorus* (*L. philenoptera Benth.*) is widely distributed throughout Africa [1,2] and invariably used medicinally. It belongs to a family of plants which frequently yield isoflavonoids [3] and accordingly the individual parts of the plant are being separately examined for phenolic constituents.

From the sodium-carbonate-insoluble fraction of the ether extract of the bark-free roots have been isolated four new closely related substances. The first, lonchocarpan (LL3) has been assigned structure (1), the second, laxifloran (LL4) [isolated as the dimethyl ether (2b)]

[1] J. M. Dalziel, 'The Useful Plants of West Tropical Africa', Crown Agents, 1948, p. 250.

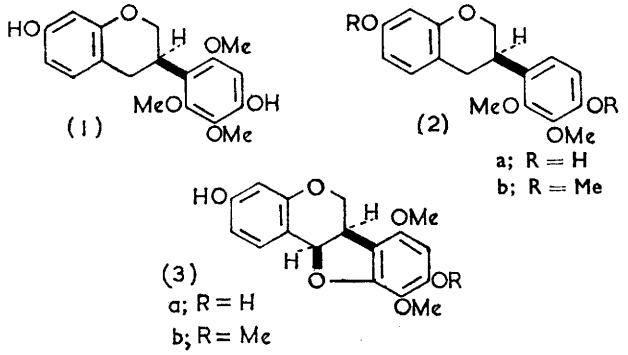
[2] J. Hutchinson and J. M. Dalziel, 'Flora of West Tropical Africa,' Crown Agents, 1958, p. 523.

[3] B. A. Bandukova, *Rastitcelnyye Resurci*, 1968, **4**, 97.

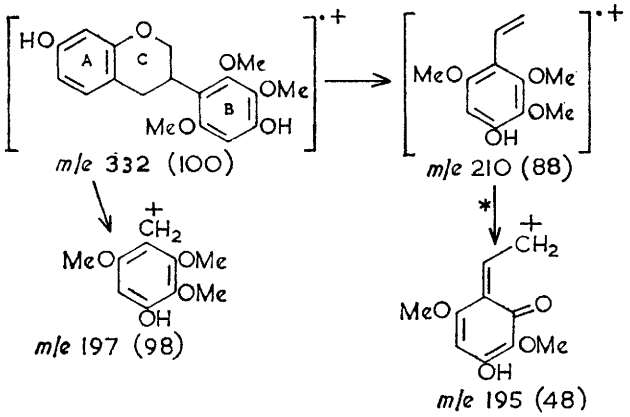
TABLE 1

	Formula	M.p.	$\lambda_{max.}$ [mμ (log ε)]	$\nu_{max.}$ ($CHCl_3$) ($cm.^{-1}$)	$[\alpha]_D$ ($CHCl_3$)
LL1	$C_{17}H_{16}O_6$	186—187°	280 (3·59), 286 (3·54)	3590, 3520, 1620, 1600, 1500	−271°
LL1 diacetate	$C_{21}H_{20}O_8$	208—210	283 (3·71)	1765, 1620, 1600, 1500	
LL1 dimethyl ether	$C_{19}H_{20}O_6$	117—118	279 (3·62), 285 (3·59)	1615, 1580, 1490, 1110	−253
LL2	$C_{18}H_{18}O_6$	183—185	280 (3·51), 286 (3·45)	3600, 1620, 1600, 1500, 1105	−240
LL2 acetate	$C_{20}H_{20}O_7$	147—148	278 (3·58)	1765, 1620, 1600, 1500	
LL3	$C_{18}H_{20}O_6$	155—157	283·5 (3·66)	3595, 3530, 1618, 1598, 1115	+56
LL3 diacetate	$C_{22}H_{24}O_8$	143—145	283 (3·70)	1755, 1605, 1590	
LL3 dimethyl ether	$C_{20}H_{24}O_6$	97—99	283 (3·8), 288 (3·71)	1620, 1600, 1585, 1490, 1110	+61·8
LL4 dimethyl ether	$C_{19}H_{22}O_5$	65—67	280 (3·55), 288 (3·44)	1620, 1583, 1490, 1110	0°, $[M]_{292}$ + 1295

has structure (2a), philenopteran (LL1) is a pterocarpan of formula (3a), and LL2 is 9-*O*-methylphilenopteran (3b). The physical constants and formulae for the natural products and their derivatives are shown in Table 1. The monomethyl ether of LL2 was identical with LL1 dimethyl ether and is not listed separately.



The u.v. spectra show that if lonchocarpan and laxifloran dimethyl ether are flavonoid in nature the heterocyclic ring must be fully reduced. The mass spectra of lonchocarpan and its derivatives agree well with the established patterns for flavans and isoflavans [4] if ring A of lonchocarpan has one hydroxy-group and ring B has one hydroxy-group and three methoxy-groups. Scheme 1 shows the main fragmentations for lonchocarpan; as (Table 2) make it clear that the substance is an isoflavan. None of the compounds have an aliphatic doublet as low as *ca.* τ 5·0, corresponding to H-2 of a flavan.[5] Table 2 also shows the n.m.r. spectra of dihydromethylphilenopteran (4), dihydropterocarpin (5), dihydrohomopterocarpin (6a), methyl dihydrohomopterocarpin (6b), and laxifloran dimethyl ether (2b).



SCHEME 1

Whilst the spectrum of (2b) fits neatly into the pattern shown by the known isoflavans, the spectra of lonchocarpan and its derivatives differ considerably in detail as regards the aliphatic protons. However it is

TABLE 2 *

N.m.r. spectra of some isoflavans

	(4)	(5)	(6a)	(6b)	LL3	Methyl LL3	Acetyl LL3	Methyl LL4
H-2	5·41 (d) J 11 5·86 (m) J *ca.* 10	5·76 (q) J_1 10 J_2 3 6·16 J_1 9 (sextet) J_2 3	5·72 (q) J_1 11 J_2 4 6·02 (t) J 9	5·68 (q) J_1 10 J_2 2 6·0 (t) J 10	5·52 (t) J 11 5·9 (m) J_1 *ca.* 11	5·44 (t) J 11 5·85 (m) J *ca.* 11	5·42 (t) J 11 5·84 (m)	5·7 (q) J_1 10 J_2 3 6·02 (t) J 10
H-3	6·1—6·5 (m)	*ca.* 6·3—6·7 (m)	*ca.* 6·2—6·7 (m)	*ca.* 6·2—6·6 (m)	6·1—6·5 (m)	*ca.* 6·1—6·4 (m)	*ca.* 6·1—6·4 (m)	*ca.* 6·2—6·7 (m)
H-4	6·64 (t) J 12 7·38br (d)	7·12br 7·20br	7·08 (d) J 4 7·16br	7·04 (d) J 4 7·15br	6·8 (t) J 12 7·45br	6·71 (t) J 12 7·38br	6·64 (t) J 12 7·2—7·4 (m)	7·06br 7·16br
OMe	6·16, 6·18 6·27, 6·28	6·31	6·30, 6·32	6·19, 6·21 6·24	6·16, 6·18 6·30	6·16, 6·18 6·20, 6·26 (2)	6·16, 6·22 6·28	6·1, 6·12 6·16, 6·24
Aromatic	3·09 (1H, d) J 9 3·50—3·70 (2H, m) 3·94 (1H, s)	3·09 (1H, d) J 8 3·4—3·8 (4H)	2·86—3·1 (2H) 3·44—3·62 (4H)	2·85—3·1 (2H) 3·45—3·65 (4H)	3·08—3·22 (1H) 3·50—3·80 (3H)	3·08 (1H, d) J 9 3·45—3·65 (2H, m) 3·72 (1H, s)	2·7—3·5 (3H, m) 3·63 (1H, s)	2·9—3·7 (4H)

* For all Tables of n.m.r. data, spectra run in $CDCl_3$ at 35° at 100 Mc./sec. with Me_4Si as internal standard; all values on τ scale, J in c./sec.

usual the more highly methoxylated fragments take most of the charge. Di-*O*-methyl-lonchocarpan has the expected peaks at *m/e* 360 (84%), 224 (100), 209 (46), 212 (22) and 211 (76) as well as peaks at *m/e* 136 (3) and 137 (4) in an otherwise clear region of the spectrum.

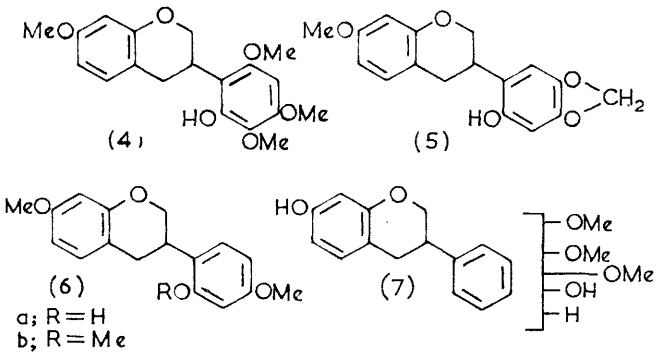
The n.m.r. spectra of lonchocarpan and its derivatives clear that the numbers of hydroxy- and methoxy-groups and aromatic and aliphatic protons are in accord with the mass spectra. In di-*O*-methyl-lonchocarpan one aromatic proton (H-5) shows as a doublet at τ 3·08 (J 9 c./sec.) coupled to H-6 at 3·56 (q), in turn *meta*-coupled to H-8 at τ 3·59 (J 3 c./sec.). The

[4] A. Pelter, P. Stainton and M. Barber, *J. Heterocyclic Chem.*, 1965, **2**, 267.

[5] A. J. Birch and M. Salahud-din, *Tetrahedron Letters*, 1964, 2211.

hydroxy-group on ring A of LL3 is therefore at C-7 and part structure (7) is established for lonchocarpan.

The arrangement of groups on the pentasubstituted ring B involves the establishment of the oxygenation pattern and then the placing of the groups in the correct relationship. The solvent-induced methoxy-proton



shifts of lonchocarpan dimethyl ether were studied to solve the first problem. The methoxy-proton shifts on changing solvent from chloroform to benzene have been shown to be useful for structure determination of simple benzene derivatives.[6] Independently of the present study it has been shown that the method has great potential in the chemistry of flavones and flavonols.[7] The compounds used,[7] however, did not show that in the presence of phenolic groups the method may be misleading as in the assignment of an incorrect structure to

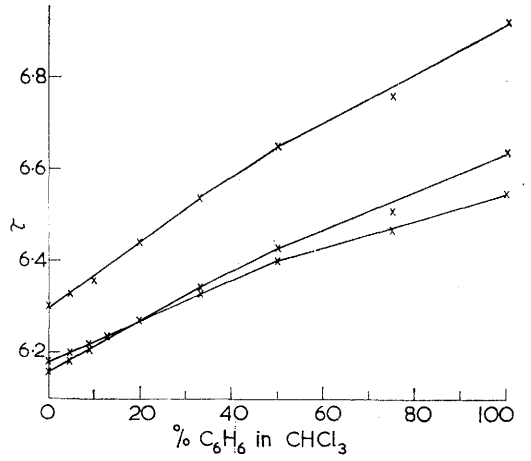
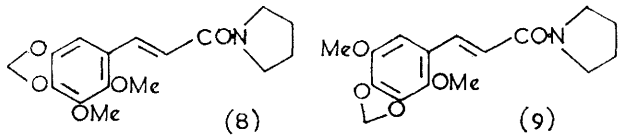


FIGURE 1 Methoxy-proton shifts for LL3

mangostin.[8,9] Figure 1 shows the methoxy-proton shifts for LL3 itself, and indicates clearly that all the methoxy-signals shift appreciably (67, 43, and 37 c./sec.), even though, owing to the heavy substitution of ring B there must be at least one methoxy-group without an *ortho*-hydrogen substituent. Further, in the case of LL3 acetate even acetylation does not overcome the difficulty, and we feel that fully methylated compounds are safest to use. Even then, however, if solvation of a separate site close to the methoxy-groups being examined occurs the results may be misleading. Thus it was not possible to distinguish between (8) and (9) for peepuloidin[10] on the basis of methoxy-proton shifts (this study is being reported elsewhere in full). One methoxy-group shows a large upfield shift even though the correct structure is



(8). The noteworthy point is that other protons in the spectrum showed larger shifts than the methoxy-groups, a sure sign of close solvation at positions other than the benzene ring.

Given these provisos however, Table 3 shows that in fully alkylated compounds, signals of methoxy-groups *ortho*- to an aromatic hydrogen atom move upfield by more than 30 c./sec. on change of solvent from chloroform to benzene, but signals of methoxy-groups lacking such a proton move by 0—20 c./sec. The blocking substituents may be any of a large variety of groups, and are not confined to other methoxy-groups.

TABLE 3 *

Methoxy-proton shifts on change of solvent from chloroform to benzene

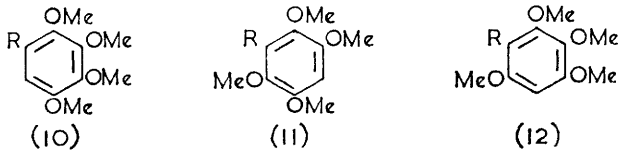
	τ Values of methoxy-groups (±1·0 c./sec.)	
	$CDCl_3$	C_6H_6
1,2-Dimethoxybenzene	6·13 (2)	6·60 (2)
1,3-Dimethoxybenzene	6·22 (2)	6·69 (2)
1,4-Dimethoxybenzene	6·24 (2)	6·66 (2)
2,4-Dimethoxybenzaldehyde	6·11, 6·14	6·79, 6·87
1,2,3-Trimethoxybenzene	6·15 (3)	6·20, 6·58 (2)
1,2,4-Trimethoxybenzene	6·07, 6·15, 6·20	6·51, 6·60, 6·64
3,4,5-Trimethoxybenzaldehyde	6·06 (3)	6·26, 6·71 (2)
3,4,5-Trimethoxybenzoic acid	6·07 (3)	6·24, 6·70 (2)
2,4,5-Trimethoxybenzaldehyde	6·03, 6·08, 6·13	6·38, 6·75, 6·81
1,2,3,5-Tetramethoxybenzene	6·16 (2), 6·22, 6·23	6·19, 6·60 (2), 6·62
1,3-Dibenzyloxy-2,5-dimethoxybenzene	6·17, 6·34	6·20, 6·68
2,3,4,6-Tetramethoxybenzaldehyde	6·05 (2), 6·10, 6·19	6·21, 6·36, 6·74 (2)
2,4-Dibenzyloxy-3,6-dimethoxybenzaldehyde	6·06, 6·18	6·25, 6·78
2,6-Dimethoxybenzoquinone	6·06 (2)	6·85 (2)
2′,4′,7-Trimethoxyflavan	6·19 (2), 6·24	6·64, 6·66, 6·78
2′,7-Dimethoxy-3′,4′-methylenedioxyflav-3-ene	6·22, 6·24	6·70, 6·89
3,9-Dimethoxypterocarpan	6·22, 6·24	6·73, 6·75

* Number of methoxy-groups in parentheses where more than one. All solutions 0·025M.

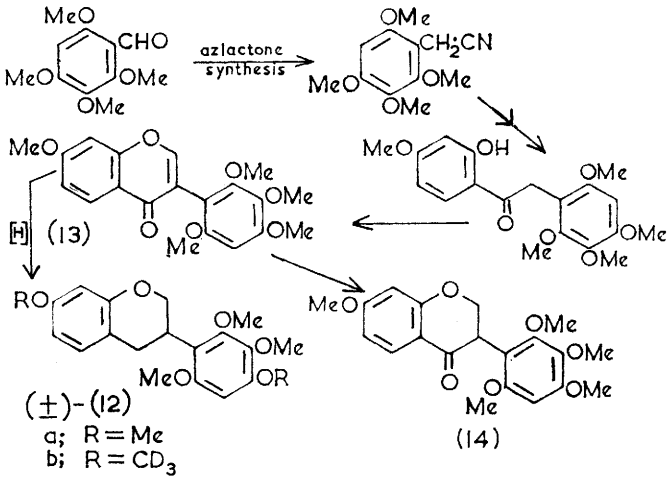
In deuteriochloroform the methoxy-groups of di-*O*-methyl-lonchocarpan show at τ 6·16, 6·18, 6·20, and 6·26(2), shifted to 6·29, 6·37, 6·59, 6·63, and 6·79 in benzene. These represent shifts of 13, 19, 37, 39, and

[6] H. M. Fales and K. S. Warren, *J. Org. Chem.*, 1967, **32**, 501.
[7] R. G. Wilson, J. H. Bowie, and D. H. Williams, *Tetrahedron*, 1968, **24**, 1407; *cf.* J. H. Bowie, J. Ronayne, and D. H. Williams, *J. Chem. Soc.* (*B*), 1967, 535.
[8] F. Scheinmann, *Chem. Comm.*, 1967, 1015.
[9] G. H. Stout, M. M. Krahn, P. Yates, and H. B. Bhat, *Chem. Comm.*, 1968, 211.
[10] C. K. Atal, P. N. Moza, and A. Pelter, *Tetrahedron Letters*, 1968, 1397.

53 c./sec. Of the three possible structures (10—12) for this compound, (10) is thus excluded and (11) is most unlikely on biogenetic grounds. Therefore



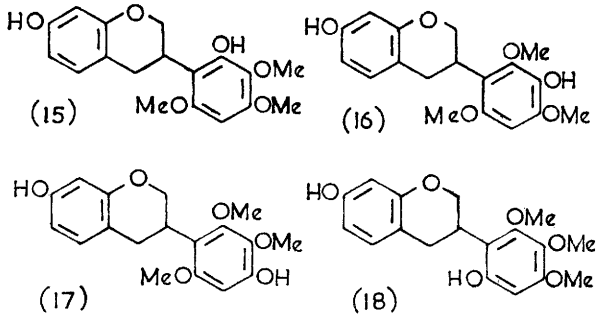
compound (12) was unambiguously synthesised by the route shown in Scheme 2. The reactions are all of known type, the only point worthy of note being the reduction of isoflavone (13 by sodium borohydride to the isoflavanone (14), this is possibly related to other constituents of *L. laxiflorus*. Catalytic hydrogenation of (13) yielded (±)-(12a), identical except for optical



SCHEME 2

activity with di-*O*-methyl-lonchocarpan. The oxygenation pattern of lonchocarpan is thus established and it remained to site the single hydroxy-group on ring B.

This could not be done by computing the position of the single aromatic proton on ring B by use of the figures of Ballantine and Pillinger.[11] The methoxy-proton

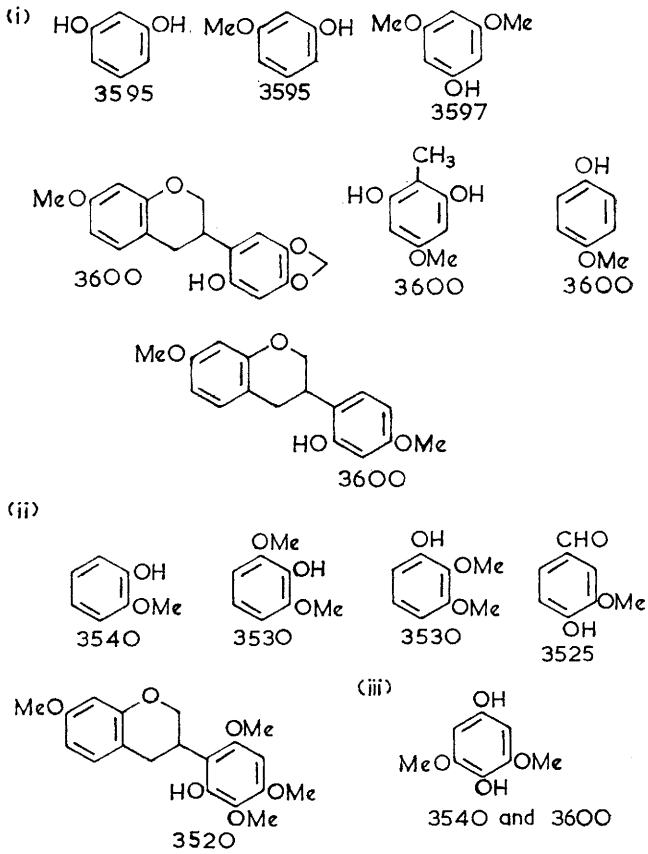


shifts of lonchocarpan were unreliable, and the acetate gave shifts of 18, 28, and 60 c./sec. The shift of 28 c./sec is such that it is not possible to decide whether or not this methoxy-group has an *ortho*-hydrogen atom.

[11] J. A. Ballantine and C. T. Pillinger, *Tetrahedron*, 1967, **23**, 1691.

Accordingly lonchocarpan was trideuteriomethylated[12] in the expectation that the product (12b) would behave exactly as (12a) on solvation, but only the original methoxy-groups could be seen. The method of trideuteriomethylation has been used in a different fashion to separate out the various methoxy-proton shifts in the flavone and flavonol series.[7] The shifts for (12b) were 14, 19, and 57 c./sec. Structures (15) and (16) are thus excluded and only (17) and (18) are left for consideration. Trideuteriomethylation should be generally useful for overcoming ambiguities associated with ambiguous methoxy-shifts of phenolic compounds.

To distinguish between (17) and (18) the i.r. spectra of a number of phenolic substances (Scheme 3) have been examined. It was clear that a hydroxy-group adjacent to a methoxy-group is weakly hydrogen-bonded to it and has an OH stretching frequency in the range 3520—3540 cm.$^{-1}$ (invariant on dilution), whereas non-hydrogen-bonded hydroxy-groups absorb at 3590—3600 cm.$^{-1}$ (variable on dilution). 1,3-Dimethoxy-2,5-dihydroxybenzene, containing both types of hydroxy-group,



SCHEME 3 I.r. absorptions (cm.$^{-1}$) for 0·03M-solutions in chloroform

shows two bands (3540 and 3600 cm.$^{-1}$). Lonchocarpan also has two bands in this region, at 3600 and 3530 cm.$^{-1}$ and hence has structure (17).

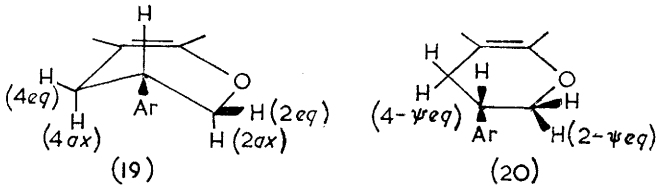
Both general methods (examination of the methoxy-

[12] K. T. van der Merwe, P. S. Steyn, and S. H. Eggars, *Tetrahedron Letters*, 1967, 2413.

proton shifts of the trideuteriomethyl derivatives and use of the solution i.r. spectra) had to be used to proceed from assignment of structure (12) to di-*O*-methyllonchocarpan to assignment of (17) to lonchocarpan itself; neither method alone was sufficient.

Laxifloran dimethyl ether has a mass spectrum with peaks at *m/e* 330, 194 (base peak), 182, 181, and 179 in agreement with structure (2b). The n.m.r. spectrum (Table 2) corresponds closely to that of methyl dihydrohomopterocarpin (6b), which it resembles, possessing only one more methoxy-group. Two *ortho*-coupled protons on ring B at τ 3·21 (d) and 3·38 (d) were shown by spin-decoupling experiments, and the usual ABC system on ring A could be identified. These results led directly to assignment of structure (2b). Confirmation was provided in that only two methoxy-groups showed large upfield shifts (42 and 50 c./sec.) on change of solvent.

The mass spectrum of the fraction rich in laxifloran and from which it was isolated as the methyl ether had an intense molecular ion at *m/e* 302 associated with fragment ions at 180 and 167. This is consistent with the view that laxifloran has one hydroxy-group on each of the two aromatic rings, and in view of the co-occurrence of lonchocarpan and laxifloran, (3a) is the most probable formulation for laxifloran itself.



The anomalous n.m.r. spectra of lonchocarpan, its derivatives, and dihydromethylphilenopteran (4), *i.e.* the 2′,6′-oxygenated isoflavans, can now be considered. If the normal conformation of the isoflavan ring is the half-chair form (19), then H-2_{eq} is not equivalent to H-2_{ax} with respect to the *p*-electrons of the adjacent oxygen atom, although they are symmetrical with respect to the C-3 aryl group. These protons show therefore as

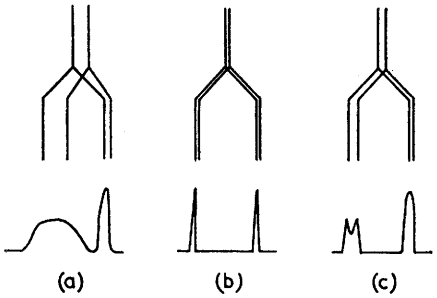
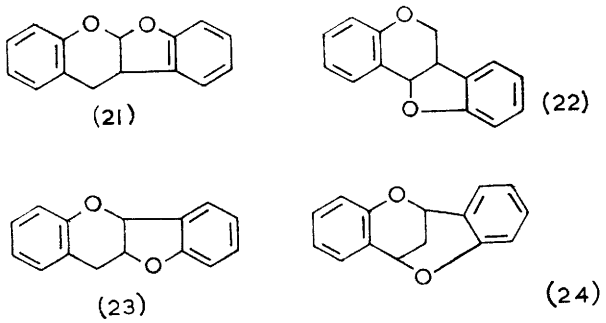


FIGURE 2 N.m.r. patterns for some standard isoflavans: (a) dihydrohomopterocarpin, methyldihydrohomopterocarpin; (b) laxifloran dimethyl ether; and (c) dihydropterocarpin, methyldihydropterocarpin

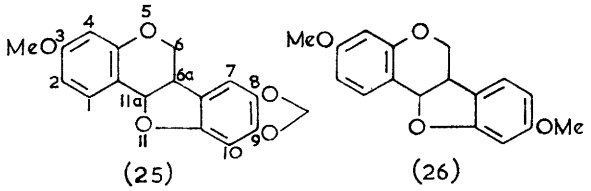
a normal ABX pattern. Two protons on C-4 however are almost symmetrical with regard to both benzene rings A and B. These protons show varying patterns approximating to an A_2B system, the particular pattern shown being very sensitive to small changes in geometry of the system and to the initial separation of the τ values of the two protons. The patterns shown in Figure 2 are for some standard (*i.e.* not 2′,6′-oxygenated isoflavan.

Models indicate that if the aromatic ring at C-3 is di-*ortho*-substituted (2′,6′) by hydroxy- or methoxy-groups then H-2_{ax} and H-4_{ax} of a half-chair form are, together, a considerable barrier to rotation. Some relief is evident if a half-boat conformation is adopted despite the eclipsing interactions (not, of course, so severe in this partly unsaturated ring containing one oxygen atom). This is illustrated in its extreme form in (20), where the protons at C-4 are highly dissymmetric with respect to the C-3 aryl group, and like the protons of C-2 are well differentiated, showing as the AB pair of an ABX system. Long-range coupling sometimes causes the rough triplet of H-$4_{\psi\text{-}eq}$ to become a sextet.

Philenopteran (LL1) and LL2 are related as parent compound and monomethyl ether. The two substances have absorption spectra very similar to those of the isoflavans previously characterised and *a priori* it seemed that the substances might be related. If this were so LL1 and LL2 must, on the basis of the molecular formulae, contain an extra ring.



The various basic possibilities retaining the flavan or isoflavan skeletons are shown in (21—24). Structures (21) and (23) may be excluded, as ready fragmentation by reverse Diels-Alder reactions would be expected under electron bombardment. In fact philenopteran and its derivatives were first distinguished from the isoflavans by their high stability in the mass spectrometer. The n.m.r. spectra (Table 4) excluded (24), the well known cyanomaclurin-type structures,[13] implying that the substances isolated have pterocarpan-type structure (22). The n.m.r. spectra of pterocarpin (25), homopterocarpin (26), LL1 and derivatives, and LL2 are shown in Table 4.



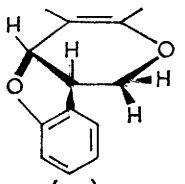
[13] G. D. Bhatia, S. K. Mukerjee, and T. R. Seshadri, *Tetrahedron*, 1966, Suppl. 7, 139; *Tetrahedron Letters*, 1966, 1717.

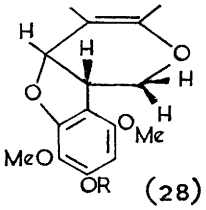
TABLE 4

N.m.r. spectra of some pterocarpans

	(25)	(26)	LL1	Methyl LL1	Acetyl LL1	LL2	Acetyl LL2
H-6$_{eq}$	5·78—5·96 (m)	5·76—5·94 (q?)	5·57 (d) J 5	5·71 (d) J 5	5·58 (m)	5·7 (d) J 5	5·54—5·8 (m)
H-6a$_{eq}$	6·1—6·8 (m)	6·2—6·7 (m)	5·6—5·9 (m)	5·8—6·8 (m)	6·0—6·4 (m)	5·8—6·2 (m)	5·8—6·5 (m)
H-6a$_{ax}$			6·1—6·4 (m)	6·4 (d) J 6		6·37 (d) J 6	
H-11a	4·63 (d) J 6	4·58 (d) J 6	4·41 (d) J 6	4·55 (d) J 6	4·42 (d) J 7	4·54 (d) J 6	4·48 (d) J 6
OMe	6·32	6·31, 6·33	6·02, 6·14	6·22, 6·24 6·25, 6·29	6·17, 6·21	6·18, 6·20 6·22	6·14, 6·16 6·18
Aromatic	2·69 (1H, d) J 9 3·34—3·7 (m)	2·64 (1H, d) J 9 2·95 (1H, d) J 9	2·52 (1H, d) J 8 3·38 (1H, q) J_1 8, J_2 3	2·58 (1H, d) J 8 3·44 (1H, q) J_1 8, J_2 3	2·44 (1H, d) J 8 3·22 (1H, q) J_1 8, J_2 3	2·62 (1H, d) J 8 3·50 (1H, q) J_1 8, J_2 3	2·42 (1H, d) J 8 3·25 (1H, q) J_1 8, J_2 3
		3·44 (1H, q) J_1 9, J_2 3 3·55—3·75 (3H, m)	3·50 (1H, d) J 3 3·81 (1H, s)	3·59 (1H, d) J 3 4·01 (1H, s)	3·29 (1H, d) J 3 3·84 (1H, s)	3·63 (1H, d) J 3 3·98 (1H, s)	3·29 (1H, d) J 3 3·94 (1H, s)

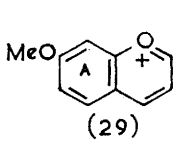
The signal for H-6$_{eq}$ is moved upfield due to an 'edge-on' effect of aromatic ring B; this is similar to that previously pointed out for the protons of the 'equatorial' series of 3,7-dioxabicyclo[3,3,0]octane lignans.[14] A thorough analysis of the n.m.r. spectra of pterocarpans appeared [15] during the present work; the conclusions were that (i) the Karplus equation does not hold in this fused system (once more the situation is similar to that in the lignans [14]), (ii) long-range coupling prevents a first-order analysis, *i.e.* $J_{6ax,11ax} = -0{\cdot}9$ to $-0{\cdot}8$ and $J_{6eq,11ax} = +0{\cdot}5$ to $+0{\cdot}7$ c./sec., and (iii) the conformation generally adopted is that shown in (27). On this basis it is clear why H-6$_{eq}$ is influenced by ring B. The spectra

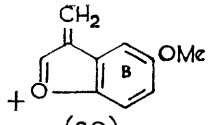

(27)


(28)

of LL1 and its derivatives indicate conformation (28), in which there is a lowering of the interaction between the 6-protons and the 7-methoxy-group. The clear differentiation between H-6$_{eq}$ and H-6$_{ax}$ follows from conformation (28) for LL1. The general pattern of the n.m.r. spectra of LL1 and its derivatives confirms their assignment as pterocarpans.

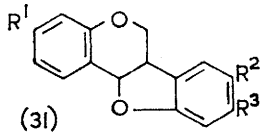
In addition to the four aliphatic protons, LL1 has two hydroxy-groups, two methoxy-groups, and four aromatic protons. In this series, unlike the isoflavans, the mass spectra cannot be used to assign the various groups to ring A and B for, as shown previously,[4] every fragment can be reasonably formulated as arising from either ring.


(29)


(30)

Thus in di-*O*-methylphilenopteran the ion at *m/e* 161 may be written as either (29) or (30).

The assignment was made by first comparing the actual position of the aromatic proton signals of mode pterocarpans (31) (each position checked by spin-decoupling experiments) with estimates based on the figures of Ballantine and Pillinger.[11] For ring B the estimated values were very close to those found, but for ring A, the H-1 signal is 21—26 c./sec. lower than computed values and 15—19 c./sec. lower for the acetates.


(31)

a; R^1 = OMe, R^2, R^3 = O·CH_2·O
b; R^1 = OAc, R^2, R^3 = O·CH_2·O
c; R^1 = OMe, R^2 = H, R^3 = OMe
d; R^1 = OAc, R^2 = H, R^3 = OMe

The H-2 signal is also low by 9—11 c./sec. in the parent substances and *ca.* 6 c./sec. in the acetates (see Table 5). These corrections were applied to calculations of the

TABLE 5

τ Values for aromatic protons of pterocarpans

Position of proton:	1	2	4	7	8	10
(31a) Obs.	2·69	3·46	3·62	3·40		3·66
Calc.	2·90	3·55	3·60	3·35		3·70
(31b) Obs.[15]	2·52	3·24	3·31	3·33		3·60
Calc.	2·70	3·30	3·35	3·35		3·70
(31c) Obs.	2·64	3·44	3·60	2·95	3·65	3·63
Calc.	2·90	3·55	3·60	2·90	3·55	3·60
(31d) Obs.[15]	2·51	3·24	3·32	2·92	3·60	3·59
Calc.	2·70	3·30	3·35	2·90	3·65	3·60

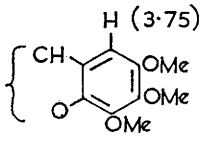
τ values for the protons of the two possibilities for philenopteran with the result shown in Scheme 4. (Double resonance experiments clearly established a 1,2,4-hydrogen pattern for one ring and the low τ value for one of these protons made it clear that this proton is not *ortho* or *para* to an oxygen atom on the ring.) The figures observed closely parallel those of type (a) with the single methoxy-group at C-3.

The possible oxygenation patterns for ring B of di-*O*-methylphilenopteran are shown in (32)—(35); the figures in parentheses are the calculated values for the appropriate proton. The observed value is τ 4·01 and structures (32) and (34) are thus excluded. As hydrogenation followed by methylation of either (33) or (35)

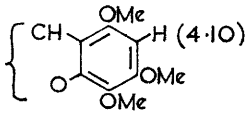
[14] A. J. Birch, P. Macdonald, and A. Pelter, *J. Chem. Soc.* (*C*), 1967, 1968.

[15] K. G. R. Pachler and W. G. E. Underwood, *Tetrahedron*, 1967, 1877.

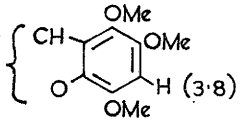
would yield dimethyl-lonchocarpan, arguments based on analogy with this compound are not relevant.



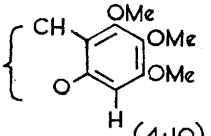
(32)



(33)

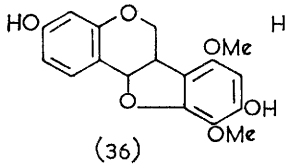


(34)

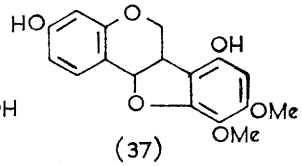


(35)

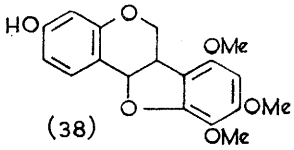
The benzene-induced methoxy-proton shifts for di-*O*-methylphilenopteran were 35, 49, and 53 c./sec. for three methoxy-groups; the other did not shift at all. Table 4), the high-field singlet on ring B remaining untouched, it is the 3-hydroxy-group that is free. This was confirmed in that the OH stretching frequency of LL2 is at 3600 cm.$^{-1}$, and LL2 is represented by (38).



(36)

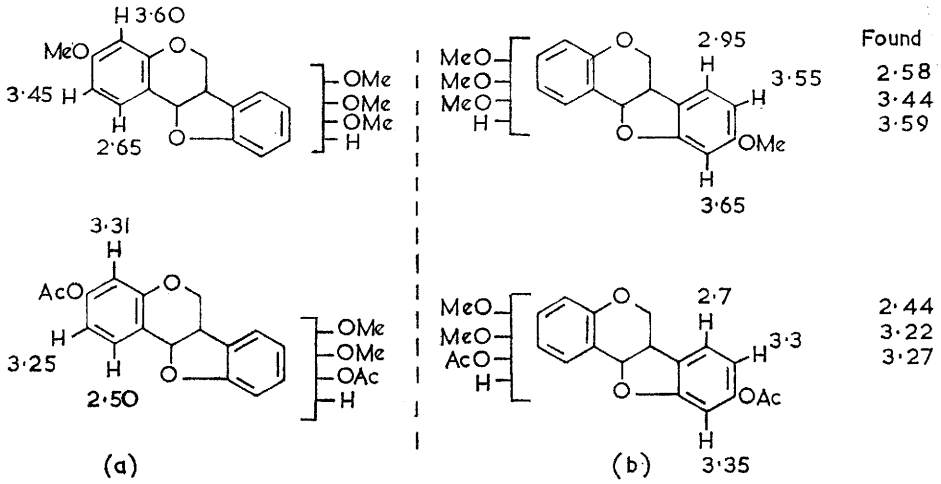


(37)



(38)

Absolute Configuration.—Following the establishment of the absolute configuration at C-11a of trifolirhizin [16]



SCHEME 4

Structure (35) is thus excluded and (33) is correct. Confirmation was provided by hydrogenolysis, which gave an isoflavan with an OH stretching frequency at 3520 cm.$^{-1}$ in accord with structure (4) derived from (33). Methylation of (4) gave lonchocarpan dimethyl ether, identical in all respects, including optical rotation, with the compound produced by methylation of lonchocarpan.

The n.m.r. spectrum of philenopteran, by comparison with that of its acetate, showed that there was one hydroxy-group on ring A and one on ring B (*cf.* peak at *m/e* 147 in the mass spectrum), that on ring A being at C-3. The solvent-induced shift of philenopteran acetate was unambiguous; one methoxy-group signal moved slightly downfield and the other moved up by 58 c./sec. It was not thought necessary to trideuteriomethylate to confirm this. The only possible structures for philenopteran are (36) and (37), and as the OH stretching frequencies are 3590 and 3520 cm.$^{-1}$, structure (36) is correct.

Compound LL2 had already been shown to be a monomethylphilenopteran, and as it is the ABC pattern of protons on ring A that is influenced on acetylation (see (7-glucosyloxy-8,9-methylenedioxypterocarpan) as (*R*) and on the assumption that the heterocyclic rings are *cis*-fused, then the absolute configurations of (−)-demethylpterocarpin and (−)-pterocarpin may be taken as (6a*R*,11a*R*). These compounds, together with all other pterocarpinoids except (+)-homopisatin and (+)-sophojaponicin, have a large negative $[\alpha]_D$ value and have been taken to have the same absolute configurations.[16] It has been pointed out however [17] that for these compounds and for the isoflavans there is a need to run o.r.d. curves below 300 mμ in order to establish definite correlations. Figure 3 shows the o.r.d. curves of (−)-homopterocarpin, (−)-pterocarpin, and (−)-philenopteran, and it seems clear that they all have the same (6a*R*,11a*R*) absolute configuration.

The derived isoflavans (−)-dihydropterocarpin and (−)-dihydrohomopterocarpin clearly have the same configuration at C-3 as laxiflorin *i.e.* (3*S*); the three curves follow a similar course between 300 and 220 mμ

[16] H. Suginome and T. Iwadare, *Experientia*, 1962, **18**, 163.
[17] D. R. Perrin and W. Bottomley, *J. Amer. Chem. Soc.*, 1962, **84**, 1919.

(Figure 4). Lonchocarpan, however, follows a very different course in this significant region and appears to have the enantiomeric configuration. This is not so,

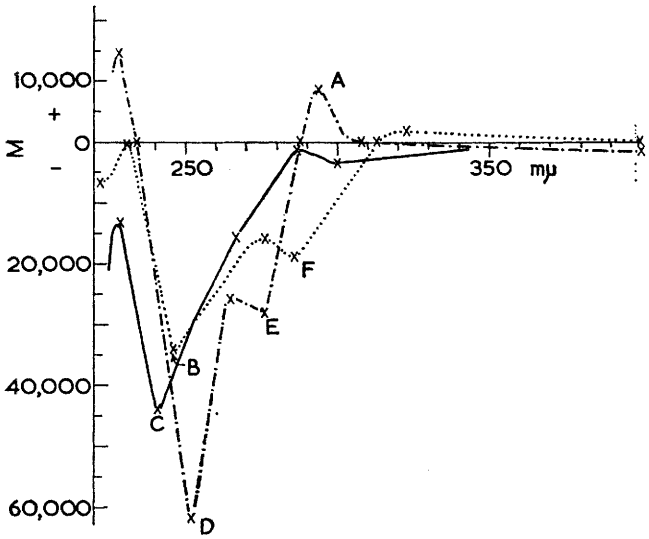


FIGURE 3 O.r.d. curves for (−)-philenopteran (——), (−)-homopterocarpin (— · — · —), and (−)-pterocarpin (· · · ·). A, +8500 (294 mμ); B, −34,000 (246 mμ); C, −43,800 (241 mμ); D, −61,000 (242 mμ); E, −28,000 (276 mμ); and F, −18,700 (286 mμ)

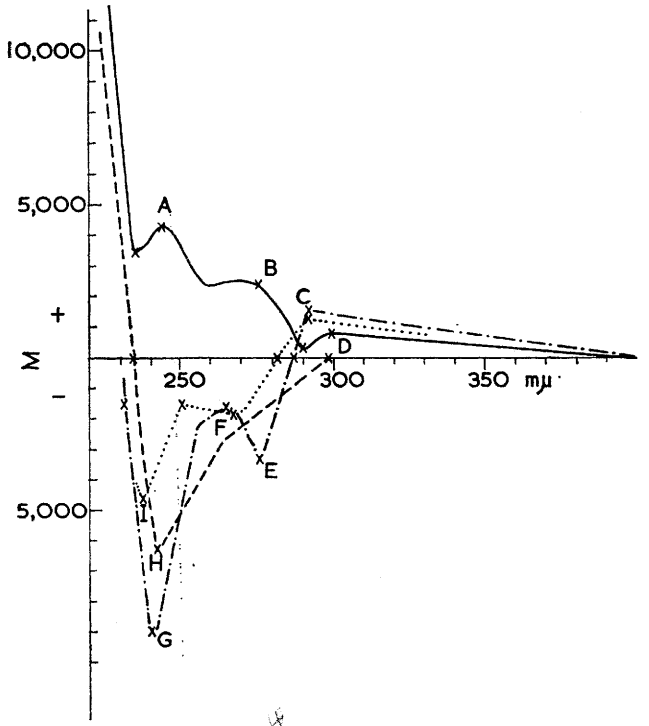


FIGURE 4...O.r.d. curves for lonchocarpan dimethyl ether (——), dihydrohomopterocarpin (— · — · —), dihydropterocarpin (– – – –), and laxifloran dimethyl ether (· · · ·). A, 4310 (244 mμ); B, 2370 (276 mμ); C, 1295 (292 mμ); D, 775 (300 mμ); E, −3300 (276 mμ); F, −1850 (267 mμ); G, −9000 (240 mμ); H, −6250 (242 mμ); and I, −4620 (238 mμ)

however, as dimethyl-lonchocarpan may be produced from philenopteran, and the absolute configuration of the latter is the same as that of (−)-pterocarpin and (−)-homopterocarpin.

The o.r.d. curve for lonchocarpan reflects the different conformation adopted by the heterocyclic ring in this compound, and this may well be related to the 'abnormal' o.r.d. curve reported by Clarke-Lewis [18] for dihydrodeoxydeguelin. In this compound the conformation of the relevant heterocyclic ring is very similar to that of lonchocarpan, the two benzene rings having nearly the same relationships. The structures of the products characterised so far are completely expressed by formulae (1), (2b), and (3b). It should be noted that all the absolute configurations in this series are fixed by the degradation of trifolirhizin to paraconic acid. The evidence used by the Japanese authors to assign the absolute configuration of this acid was very indirect and in contradiction to the assignment given by Toccanne and Asselineau.[19] Very recently these workers reversed their assignment, but the method used involved a long series of reactions and further confirmation would be welcome.

EXPERIMENTAL

The powdered, dried, debarked roots of *L. laxiflorus* (2·7 g.) were placed in portions (300 g.) in a Soxhlet extractor, and extracted with ether for 24 hr. The combined extracts were concentrated to 200 ml., at which point solid (A) separated, and was filtered off. The filtrate was extracted successively with 10% sodium hydrogen carbonate (5 × 50 ml.), ice-cold 5% sodium carbonate (5 × 50 ml.), and ice-cold 5% sodium hydroxide (5 × 50 ml.). Each extract was neutralised rapidly with ice-cold dilute hydrochloric acid and extracted with ether. The ether extracts were dried ($MgSO_4$), filtered, and evaporated; the residues consisted of (A) a non-aromatic solid (350 mg.), (B) sodium hydrogen carbonate-soluble (3 g.), (C) sodium carbonate-soluble (6 g.), (D) sodium hydroxide-soluble (1·6 g.), and (E) neutral (and basic) fraction (8 g.).

Fraction (*D*).—The sodium hydroxide-soluble portion (1·1 g.) was dissolved in benzene (5 ml.) and carefully placed on a silicic acid (Koch–Light) column (150 g.). The elution was followed by i.r. spectroscopy and t.l.c. on the 50 ml. fractions, with the results shown in Table 6.

TABLE 6

Sample	Fraction	Eluant *	Wt. (mg.)	T.l.c.	I.r.
1	1—4	B	207	1 spot	Non-benzenoid
2	5—10	1% C–B	177	2 spots	Non-benzenoid
3	11—16	2% C–B	165	3 spots	Non-benzenoid
4	17—21	5% C–B	69	4 spots	Non-benzenoid
5	22—29	10% C–B	89	5 spots	Non-benzenoid
6	30—53	20% C–B	60	4 spots	Complex-trace of benzenoid
7	54—80	40% C–B	130	3 spots	Benzenoid
8	81—90	50% C–B	110	2 spots	Benzenoid
9	91—126	C	40	Not resolved	Complex
10	127—138	E	35	Not resolved	Complex

* B, benzene; C, chloroform; E, ethanol.

T.l.c. of samples 7 and 8. These fractions run mainly as one spot, R_F 0·35 in each case, on silica gel H thin-layer plates in benzene–ethyl acetate–formic acid (17 : 2 : 1). The spots absorb u.v. light and give brown ferric chloride

[18] J. W. Clarke-Lewis, I. Dainis, and G. C. Ramsay, *Austral. J. Chem.*, 1965, **18**, 1035.
[19] J. Tocanne and C. Asselinau, *Bull. Soc. chim. France*, 1968, 2103.

reactions. The main component from each sample was isolated by preparative t.l.c. to give from sample **7**, 110 mg., and from sample **8**, 99 mg.

Acetylation of sample 8. Sample 8 (50 mg.) was dissolved in dry pyridine (1 ml.) and the solution was treated with acetic anhydride (5 ml.) and left at 23° for 24 hr. The solution was then poured into ice–water (25 ml.) and kept at 0° for 2 hr. Crystals were then filtered off (51·3 mg.) and gave colourless needles (30 mg.), m.p. 180—195° (from ethanol). The m.p. was not sharpened by further recrystallisation.

The product from two such sequences was purified by t.l.c. [silica gel H in benzene–ethyl acetate (9 : 1)], running each plate three times. Two bands could be discerned; these were removed and extracted with chloroform. The extracts were evaporated to give (*a*) philenopteran acetate (R_F 0·8) as white *needles* (44 mg.), m.p. 208—210° (from ethanol) (Found M^+, 400·1157. $C_{21}H_{20}O_8$ requires 400·1158 *), *m/e* 400 (70%), 358 (56), 316 (100), 315 (17), 301 (32), 285 (13), and 147 (21) and (*b*) 9-*O*-methylphilenopteran acetate (R_F 0·75) as white *needles* (13 mg.), m.p. 145—147° (from aqueous ethanol) (Found: M^+, 372·1197. $C_{20}H_{20}O_7$ requires 372·1209), *m/e* 372 (86%), 330 (100), and 315 (57).

Hydrolysis of philenopteran acetate. The acetate (44 mg.) in ethanol (2 ml.) was treated with 10% aqueous alcoholic potassium carbonate (10 ml.). The mixture was set aside at room temperature for 24 hr., then diluted with water (10 ml.), neutralised with dilute hydrochloric acid, and extracted with chloroform (3 × 25 ml.) to yield crude philenopteran, which gave colourless *needles*, m.p. 186—187° (from chloroform), $[\alpha]_D^{23}$ −271° ($CHCl_3$) (Found: M^+, 316·0949. $C_{17}H_{16}O_6$ requires 316·0947), *m/e* 316 (100%), 301 (46), 286 (14), and 147 (15).

Hydrolysis of 9-O-*methylphilenopteran acetate.* A similar hydrolysis of this acetate (13 mg.) yielded 9-*O*-methylphilenopteran (9 mg.) as *needles*, m.p. 183—185° (from aqueous ethanol), $[\alpha]_D^{23}$ −240° ($CHCl_3$) (Found: M^+, 330·110856. $C_{18}H_{18}O_6$ requires 330·110326), *m/e* 330 (100%), 329 (10), 315 (31), 221 (2), 208 (3), and 147 (10).

Sample 8 acetate (30 mg.) was hydrolysed as described before to yield a product (25 mg.) as a film. This was taken up in dry methanol (1 ml.) and treated for 24 hr. at room temperature with an excess of ethereal diazomethane. After evaporation of the solvent the crude product (30 mg.) gave only a single spot on a thin-layer plate in benzene–ethyl acetate (9 : 1). The mass spectrum showed only two prominent peaks, *m/e* 344 and 329, with a metastable peak (*m** 314·7) for the transition to *m/e* 329. No mixture was apparent, so the product was crystallised from ethanol to yield philenopteran dimethyl ether as white *needles* (20 mg.), m.p. 117—118°, $[\alpha]_D^{23}$ −253° ($CHCl_3$) (Found: C, 66·55; H, 6·2%; *M**, 344·1262. $C_{19}H_{20}O_6$ requires C, 66·25; H, 5·8%; *M*, 344·1260), *m/e* 344 (100%), 343 (10), 329 (33), 221 (2), 208 (4), and 161 (14).

Hydrogenolysis of philenopteran dimethyl ether (33). Compound (33) (12 mg.) was dissolved in ethanol (10 ml.) and acetic acid (1 ml., and 10% palladium–charcoal (15 mg.) was added. Hydrogenation at room temperature and pressure was stopped after 2 hr. (uptake 1 mol. equiv.). The catalyst and solvent were removed to yield 2′-hydroxy-3′,4′,6′,7-tetramethoxyisoflavan (9 mg.) as *crystals*, m.p. 47—50° (from methanol) (Found: M^+ 346·1418. $C_{19}H_{22}O_6$ requires 346·1416), $\nu_{max.}$ ($CHCl_3$) 3520, 1617, 1598, and 1580 cm.$^{-1}$, *m/e* 346 (55%), 210 (100), 198 (26), 197 (82), 195 (57), 167 (64), 163 (38), and 137 (28).

* Other physical data for these compounds are in Table 1.

Methyldihydrophilenopteran dimethyl ether (*lonchocapan dimethyl ether*) (12). The product from the preceding hydrogenolysis (7 mg.) was taken up in methanol and methylated with an excess of ethereal diazomethane at room temperature for 24 hr. The solvents were removed and the product was purified by preparative t.l.c. [silica gel H, benzene–ethyl acetate (9 : 1)] to give (3S)-2′,3′,4′,6′,7-*pentamethoxyisoflavan* (6 mg.) (lonchocarpan dimethyl ether), m.p. 96—99° (from ethanol), mixed m.p. with authentic lonchocarpan dimethyl ether 96—99°, $[\alpha]_D^{23}$ +61° ($CHCl_3$), $\lambda_{max.}$ (EtOH) 283 (log ε 3·80) and 288 (3·72) mμ, $\nu_{max.}$ ($CHCl_3$) 1620, 1600, 1585, 1490, and 1110 cm.$^{-1}$ (Found: M^+ 360·1562. $C_{20}H_{24}O_6$ requires 360·1573).

Purification of Sample 7.—*Acetylation.* The mixture (50 mg.) was taken up in dry pyridine and acetic anhydride (5 ml.) was added. Treatment as for sample 8 yielded mixed acetates (42 mg.). Preparative t.l.c. on silica gel H in benzene–ethyl acetate (9 : 1) (each plate run three times) gave three bands: (i) R_F 0·8 (5 mg.), shown by mass spectrometry to consist of a mixture of philenopteran diacetate (*m/e* 400), LL6 diacetate (*m/e* 370), and LL4 diacetate *m/e* 386; (ii) R_F 0·75 (6 mg.), shown to be a mixture of 9-*O*-methylphilenopteran acetate (*m/e* 372), LL5 diacetate (*m/e* 430), and LL7 diacetate (*m/e* 446); and (iii) R_F 0·7 (26 mg.), *lonchocarpan diacetate* (*m/e* 416), crystallised from ethanol to yield 23 mg., m.p. 143—145° (Found: M^+, 416·1468. $C_{22}H_{24}O_8$ requires 416·1471), *m/e* 416 (30%), 374 (55), 332 (15), 210 (82), and 197 (100).

Methylation. Sample 7 (50 mg.) was taken up in dry methanol (2 ml.) and set aside with an excess of ethereal diazomethane for 24 hr. Removal of the solvents left crude methyl ethers (55 mg.), purified by t.l.c. in the same system as the mixed acetates (each plate run four times) to give (i) R_F 0·85 (5 mg.), *laxifloran dimethyl ether*, m.p. 65—67°, $[\alpha]_D^{23}$ 0° (Found: M^+, 330·145736. $C_{19}H_{22}O_5$ requires 330·146720), *m/e* 300 (55%), 194 (100), 182 (40), 181 (26), 179 (58), 167 (10), and 151 (19); (ii) R_F 0·80 (40 mg.), *lonchocarpan dimethyl ether*, m.p. 97—99° (from ethanol), $[\alpha]_D^{23}$ +61·8° ($CHCl_3$) (Found: C, 66·7; H, 6·6%; M^+, 360·1584. $C_{20}H_{24}O_6$ requires C, 66·65; H, 6·65%; *M*, 360·1573), *m/e* 360·158442(84%), 224·104847(100), 212·102616(22), 211·095958(76), 209·081181(46), 197·080536(9), 181(6), 180(10), 166(6), 149(5), 137(4), and 136 (3); and (iii) R_F 0·75 (6 mg.). The mass spectrum showed (iii) to be a mixture of philenopteran dimethyl ether (*m/e* 344), LL5 dimethyl ether (*m/e* 374), LL6 dimethyl ether (*m/e* 314), and LL7 dimethyl ether (*m/e* 390).

Lonchocarpan. The pure diacetate (23 mg.) was hydrolysed in the same way as philenopteran diacetate to yield white *plates* of lonchocarpan, m.p. 155—157° (from aqueous ethanol), $[\alpha]_D$ +56° (Found: M^+, 332·1248. $C_{18}H_2O_6$ requires 332·1259), *m/e* 332·124785 (100%), 210·088578 (88), 198·089202 (25), 197·082345 (98), and 195·065728 (48).

Lonchocarpan bistrideuteriomethyl ether. Lonchocarpan (7 mg.) was dissolved in pure, dry dioxan (5 ml.) and deuterium oxide (3 drops) was added. The solution was added to a solution (1 ml.) of diazomethane in dry dioxan containing a few drops of deuterium oxide and the mixture was set aside at room temperature for 24 hr. The solvents and excess of diazomethane were removed and the product gave crystals (5 mg.), m.p. 99—100° (from ethanol), $\nu_{max.}$ 2220, 2160, 2120, 2090, 1620, 1595, and 1585 cm.$^{-1}$.

2,3,4,6-*Tetramethoxyphenylacetonitrile*.— 2,3,4,6-Tetramethoxybenzaldehyde [20] (12 g.), benzoylglycine (12 g.) and anhydrous sodium acetate (4·8 g.) were intimately mixed and treated with acetic anhydride (28 ml.) on a steam-bath for 2 hr. Water (40 ml.) was added to the cooled mixture, which was set aside for another 2 hr. The azlactone was then filtered off and gave yellow *crystals* (11 g.), m.p. 123—124° (from ethanol), $\lambda_{max.}$ (EtOH) 232s (log ε 4·10), 270 (3·99), 280 (3·99) and 402 (4·27) mμ, $\nu_{max.}$ 1790, 1660, 1595, and 1565 cm.$^{-1}$ (Found: C, 64·8; H, 5·0; N, 3·6. $C_{20}H_{19}NO_6$ requires C, 65·05; H, 5·15; N, 3·8%).

The azlactone was heated under reflux with 12% aqueous sodium hydroxide (90 ml.) for 6 hr., and the solution was then saturated with sulphur dioxide with stirring. The precipitated benzoic acid was filtered off and the filtrate was heated with conc. hydrochloric acid (45 ml.) on a water-bath for 4 hr. The pyruvic acid separated as an oil (9 g.) which was not characterised but converted into the oxime with hydroxylamine hydrochloride (9 g.) in 10% aqueous sodium hydroxide (120 ml.) at 50—55° for 24 hr. The product was precipitated with conc. hydrochloric acid to yield **2,3,4,6-*tetramethoxyphenylpyruvic acid oxime*** (8·6 g.), m.p. 111—112° (from benzene–light petroleum), $\lambda_{max.}$ (EtOH) 282 mμ (log ε 3·33), $\nu_{max.}$ ($CHCl_3$) 3220, 2520, 1700, 1650, and 1600 cm.$^{-1}$ (Found: C, 52·5; H, 5·9; N, 4·6. $C_{13}H_{17}NO_7$ requires C, 52·15; H, 5·7; N, 4·7%).

The oxime was treated with acetic anhydride (40 ml.) at room temperature and after evolution of carbon dioxide ceased, water (100 ml.) was added. Neutralisation with solid sodium carbonate precipitated **2,3,4,6-*tetramethoxybenzonitrile***, which gave colourless needles (3·6 g.), m.p. 85° (from ethanol) (Found: C, 60·6; H, 6·7; N, 5·8. $C_{12}H_{15}NO_4$ requires C, 60·8, H, 6·3; N, 5·9%), $\lambda_{max.}$ 255 (log 3·92) and 281 (3·37) mμ, $\nu_{max.}$ 2245, 1600, and 1500 cm.$^{-1}$.

2,4-*Dihydroxy*-2′,3′,4′,6′-*tetramethoxydeoxybenzoin*.—To a solution of 2,3,4,6-tetramethoxybenzyl cyanide (20 g.), and resorcinol (20 g.) in dry ether (400 ml.) was added anhydrous zinc chloride (10 g.), and the mixture, at 0°, was saturated with dry hydrogen chloride gas. It was then left for 3 days at room temperature, the ether was decanted, and the residue was washed with fresh dry ether and heated with water (100 ml.) at 100° for 3 hr. The product gave white *plates* (14·8 g.), m.p. 188—189° (from ethanol) (Found: C, 62·1; H, 5·9. $C_{18}H_{20}O_7$ requires C, 62·05, H, 5·75%), $\lambda_{max.}$ (EtOH) 228 (log ε 4·25), 278 (4·24), and 313 (3·96) mμ, $\nu_{max.}$ (Nujol) 3280, 1640, 1597, and 1500 cm.$^{-1}$.

2-*Hydroxy*-2′,3′,4,4′,6′-*pentamethoxydeoxybenzoin*.— 2,4-Dihydroxy-2′,3′,4′,6′-tetramethoxydeoxybenzoin (12 g.) in methanol (20 ml.) was treated with an excess of ethereal diazomethane. After 24 hr. solvents were removed and the product gave white *plates* (11 g.), m.p. 148—149° (from ethanol) (Found: C, 62·9; H, 6·0. $C_{19}H_{22}O_7$ requires C, 62·95; H, 6·1%), $\lambda_{max.}$ (EtOH) 228 (log ε 4·27), 274 (4·28), and 314 (3·93) mμ, $\nu_{max.}$ (Nujol) 1635, 1620, 1600, and 1503 cm.$^{-1}$.

2′,3′,4′,6′,7-*Pentamethoxyisoflavone* (13).—The ketone from the previous reaction (5 g.) in anhydrous ethyl formate (350 ml.) was added to powdered sodium (10 g.) at 0°. The solution was well stirred for 2 hr. then left at 0° for 2 days. Iced water (100 ml.) was carefully added, and the solution was acidified (dilute hydrochloric acid) and extracted with ether (2 × 200 ml.). Removal of the solvent left a residue that was treated with conc. hydrochloric acid (5 ml.) on a water bath for 5 min. Water (20 ml.) was added and solid sodium hydrogen carbonate until the mixture was neutral. The organic matter was taken up in ether, and the extracts were dried, filtered, and evaporated. The product gave colourless *needles* (4·1 g.), m.p. 158—159° (from ethanol) (Found: C, 64·4; H, 5·3. $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%), $\lambda_{max.}$ (EtOH) 238 (log ε 4·45), 247 (4·41), 288 (4·13), and 303sh (4·05) mμ, $\nu_{max.}$ (Nujol) 1640, 1615, 1570, and 1495 cm.$^{-1}$, *m/e* 372 (100%), 357 (39), 341 (90), 329 (27), 311 (48), 299 (19), 243 (20), 200 (16), and 151 (26).

2′,3′,4′,6′,7-*Pentamethoxyisoflavan* (12a).—The isoflavone (13) (0·5 g.), was dissolved in ethanol (100 ml.) containing acetic acid (2·5 ml.) and 10% palladium–charcoal (250 mg.) was added. The solution was hydrogenated at room temperature and pressure for 3 hr. The catalyst was filtered off and the solvent removed from the filtrate. The product was chromatographed on neutralised alumina to give the *isoflavan* (12a) (390 mg.), m.p. 101—102° (from ethanol) (Found: C, 66·6; H, 6·8%; M^+, 360·1562. $C_{20}H_{24}O_6$ requires C, 66·65; H, 6·65%; *M*, 360·1573), $\lambda_{max.}$ (EtOH) 283 (log ε 3·80), 288sh (3·71) mμ, $\nu_{max.}$ (film) 1620, 1600, 1585, and 1505 cm.$^{-1}$, *m/e* 360 (30%), 224 (72), 212 (15), 211 (57), 209 (100), 197 (10), 181 (20), 166 (32), 151 (24), 149 (9), 137 (12), and 136 (19).

2′,3′,4′,6′,7-*Pentamethoxyisoflavanone* (14).—(i) The isoflavone (13) (100 mg.) was added to ethanol (10 ml.) containing sodium borohydride (30 mg.). The mixture was stirred for 24 hr. at room temperature, diluted with water (20 ml.), acidified with acetic acid, and extracted with ether (3 × 30 ml.). The extract was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by preparative t.l.c. [silica gel H in benzene–ethyl acetate–formic acid (15 : 4 : 1)] to yield the *isoflavanone* (13) as colourless *needles* (61 mg.), m.p. 119—120° (from ethanol) (Found: C, 63·9; H, 6·0%; M^+, 374·1376. $C_{20}H_{22}O_7$ requires C, 64·15; H, 5·9%; *M*, 374·1366), $\lambda_{max.}$ 227 (log ε 4·32), 272 (4·21), and 310 (3·89) mμ, *m/e* 374 (29%), 224 (100), 209 (91), 181 (16), 166 (26), 151 (23), 150 (15), and 122 (20), $\nu_{max.}$ 1680, 1605, and 1580 cm.$^{-1}$.

(ii) The isoflavone (13) (100 mg.) in ethanol (20 ml.) was hydrogenated over 10% palladium–charcoal (35 mg.) until 1 mol. of hydrogen had been absorbed, to give, after the usual purification, the isoflavanone (14) (65 mg.), identical with the product from borohydride reduction.

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[20] E. Späth and Z. Jerzmanowska-Sienkiewiczowa, *Ber.*, 1937, **70**, 698.