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^{13}C NMR OF PTEROCARPANS

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Abstract—^{13}C NMR spectra of eight pterocarpans are reported. Assignments are based on multiplicities and second-order features in off-resonance decoupled spectra and on chemical shifts in model compounds. Comparison of the degree of long-range (C, H) coupling in ^{1}H-coupled spectra is found useful.

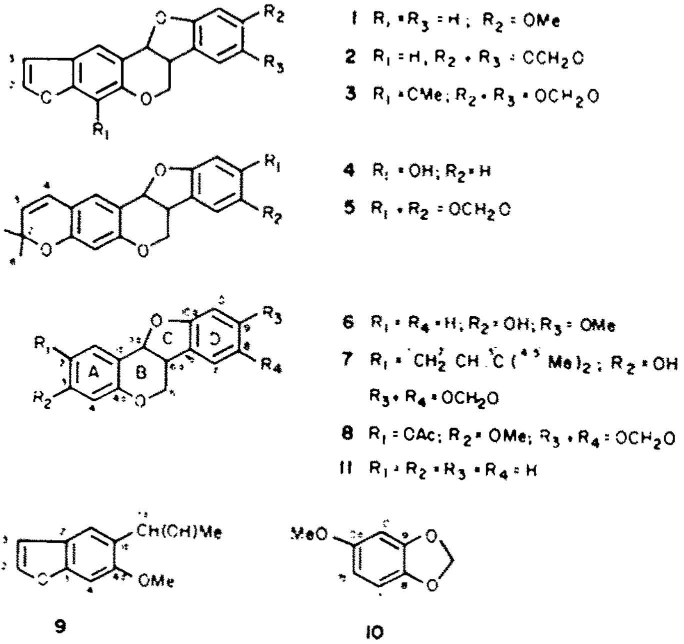
INTRODUCTION

Pterocarpans are found mainly in the heartwood of tropical genera of the Leguminosae including some outside the sub-family Lotoideae.[1] In other leguminous plants, pterocarpans are often found in the roots (e.g. in *Neorautanenia*[2] and *Lonchocarpus*[3]). In pterocarpan structure determinations extensive use has been made of ^{1}H NMR[4,5] but interpretation may not be straightforward and can be ambiguous, for example, in giving aromatic substitution patterns. It may be anticipated that the greater chemical shift information in ^{13}C spectra will be of help in structure determinations once the background data are available. To obtain this information we have undertaken a study of the ^{13}C NMR of neodunol **1**, neodulin **2**, ficinin **3**, neorautenol **4**, neorautenaan **5**, medicarpan **6**, edunol **7**, 2-acetoxypterocarpin **8** and two model compounds **9** and **10** (Fig. 1).

Pterocarpans contain the coumaranochroman ring system **11**, (6a,11a - dihydro - 6H - benzofuro[3,2-*c*][1]benzopyran) and those studied here have substituents on only the A- and D-rings. The D-ring modifications are relatively minor; replacement of a 9-hydroxy by a 9-methoxy or 8,9-bridging methylene dioxy group. The A-ring modifications are more profound involving a variety of substituents or the formation of a further ring.

Proton noise-decoupled (PND) and single-frequency off-resonance decoupled (SFORD) ^{13}C spectra were recorded for all compounds and in addition ^{1}H-coupled ^{13}C spectra were obtained for the pterocarpans **4**, **5** and **7** and the model compounds **9** and **10**.

A secondary characteristic of the SFORD spectra, useful here in assignment of aromatic and olefinic proton-bearing carbons, is that second-order features[6] were shown if the directly bonded proton is strongly coupled to another proton (at least an ABX, X = ^{13}C system). Where the directly bonded proton gives a singlet in the ^{1}H-spectrum the SFORD signal for the carbon (part of an AX system) was always a simple sharp doublet. The



1 $R_1 = R_3 = H$; $R_2 = OMe$

2 $R_1 = H$, $R_2 + R_3 = OCH_2O$

3 $R_1 = OMe$; $R_2 + R_3 = OCH_2O$

4 $R_1 = OH$; $R_2 = H$

5 $R_1 + R_2 = OCH_2O$

6 $R_1 = R_4 = H$; $R_2 = OH$; $R_3 = OMe$

7 $R_1 = CH_2CH{=}C(Me)_2$; $R_2 = OH$
$R_3 + R_4 = OCH_2O$

8 $R_1 = OAc$; $R_2 = OMe$; $R_3 + R_4 = OCH_2O$

11 $R_1 = R_2 = R_3 = R_4 = H$

9 **10**

Fig. 1. The pterocarpans and model compounds with numbering scheme.

appearance of the second-order features depends on the residual coupling and the ^{1}H chemical shifts involved, but when observed under the usual high-power decoupling conditions, show that the system is more complex than AX.

Increasing use is being made of ^{1}H-coupled spectra even for complex natural products.[7] With the spectral resolution usually attained in routine work on such compounds only the larger J(C,H) are observed. Proton-bearing benzenoid carbons therefore show ^{3}J(C,H) to *meta* protons[8] (~ 7 Hz) and slightly smaller (~ 5 Hz) to *peri* protons[9] reflecting the respective dihedral angles of 180 and 0°. Intramolecularly hydrogen-bonded OH protons may also give rise to ^{3}J(C,H) in phenols.[7] Other substituent protons will show significant ^{3}J(C,H), viz. the 5 Hz average coupling[10] of toluene methyl protons to C-2, if the dihedral angle is favourable. Quaternary benzenoid carbons show two- and three-bond couplings.[9]

DISCUSSION

Assignments

C-6, C-6a, C-11a, methyl, methoxyl and methylene dioxy carbons are all assigned directly from their characteristic chemical shifts and SFORD multiplicities as are C-2' of the furan moiety and the quaternary C-2' of compounds **4** and **5**. The appearance of the furanoid C-3' signal on SFORD is characteristically complex although this could be due to either second-order effects or the incomplete collapse of the large ^{2}J(C,H) which in the benzofuran **9** is 12.7 Hz. Assignment of the carbons of the isopentenyl side-chain in **7** is made by comparison with data for the analogous carbons of acyclic terpenes[11] and other natural products.[12,13]

The remaining carbons are all benzenoid or olefinic but for the purposes of assignment can be divided into three groups: proton-bearing carbons, quaternary carbons bonded to oxygen, and quaternary carbons not bonded to oxygen.

Proton-bearing carbons. Assignments for both A- and D-ring carbons in compounds **1**, **2** and **3** come unambiguously from the shift or lack of shift accompanying the A- and D-ring modifications. For all the other pterocarpans the D-ring assignments are therefore secure. All A-ring carbons of **6**, **7** and **8** but only C-4 in **4** and **5** are assigned on the basis of the well documented[14] shielding effect of *ortho* oxygen functions.

Further evidence is found in the ^{1}H-coupled spectra (Fig. 2) of compounds **4** and **5**. In these spectra the sharpest lines have widths of about 4 Hz due to small unresolved long-range couplings and the limited computer memory size. In the spectrum of **5** the doublets for C-4, C-7 and C-10 are of this line-width whereas C-1 (and C-3' and C-4') show further splitting. In the spectrum of **4**, in which a proton is now present on C-8, C-4 and C-7 remain sharp whereas C-8 and C-10 are more extensively coupled, and C-1 (and C-3' and C-4') are unchanged. The simplest interpretation is that C-10 and C-8 show coupling to the *meta* protons H-8 and H-10 respectively. The alternative explanation, that the new coupling is from the hydroxy proton,[7] would give the same assignment confirmation but is unlikely for this compound. Interestingly, C-7 shows no long-range coupling although it is three bonds away from H-6a and this can be attributed to the unfavourable dihedral angle in the coumaranochroman system.[4] Long-range splittings in the spectra of **9** and **10** are shown in Table 1. Assignment of the coupling, in cases of ambiguity, is based on the large ^{2}J(C,H) of furanoid carbons[8] and the fact that C-1 in the 2',3'-dihydro derivative of **9** shows no long-range coupling.

No distinction between C-1, C-3' and C-4' of **4** and **5** can be made from the degree of coupling but in the

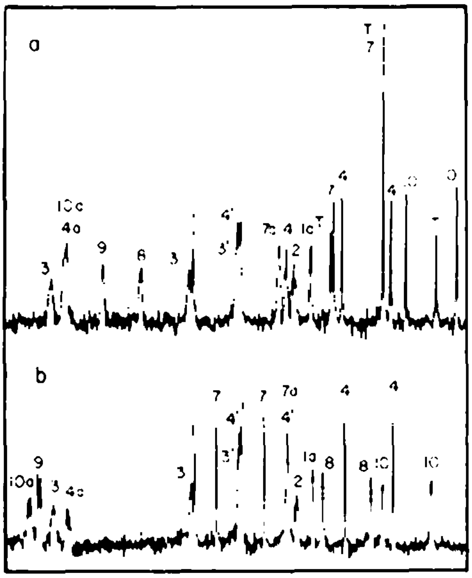


Fig. 2. ^{1}H-coupled ^{13}C spectra of the aromatic region (a) Compound **5**. T marks methylene dioxy triplet; (b) Compound **4**.

Table 1. ^{13}C data* for pterocarpans and model compounds. C-1–C-11a

	C-1	C-1a	C-2	C-3	C-4	C-4a	C-6	C-6a	C-7a	C-7	C-8	C-9	C-10	C-10a	C-11a
1	123.1	117.2	121.8	154.8	99.0	153.3	66.5	39.4	119.7	124.9	106.1	160.5	96.2	160.2	78.5
2	122.9	117.2	121.8	154.7	98.9	153.3	66.4	39.9	118.0	104.9	141.1	147.3	92.8	153.5	78.3
3	116.2	118.6	122.8	146.7	133.3	144.9	66.7	39.9	118.0	105.1	141.1	147.4	92.9	153.6	78.5
4	128.5	113.0	115.6	156.0	103.7	153.7	66.0	38.8	117.3	124.9	107.4	158.4	97.4	159.7	77.4
5	128.4	113.0	115.6	156.0	103.7	153.7	65.8	39.6	118.1	105.0	141.1	147.5	93.0	153.7	77.7
6	132.0	111.3	109.7	158.7	102.9	156.4	65.5	39.3	119.4	125.0	106.0	160.6	96.3	160.4	78.1
7	130.8	110.7	121.6	155.9	102.4	153.9	65.6	39.6	118.2	104.9	140.8	147.2	92.9	153.6	78.0
8	124.2	112.1	133.9	152.0	101.4	154.0	66.0	39.6	118.1	105.3	141.2	147.5	93.2	153.6	77.4
9	117.1	129.6	119.4	154.4	94.0	154.2									63.9
10									104.8	107.7	141.4	148.2	97.2	155.1	

*Chemical shifts in ppm from TMS.Couplings in Hz.
Couplings in **9** and **10**
9 (C-1, H-3') = 4.0; (C-2', H-3') = 10.8; (C-3',H-2') = 12.7; (C-3', H-1) = 2.9;
10 (C-7a, H-10) = 4.6; (C-10, H-7a) = 6.0

Table 2. ^{13}C data for pterocarpans and model compounds. Substituent carbons

	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	OCH_2O	OMe	CO	Me
1		145.6	106.1					55.2		
2		145.6	106.1				100.8			
3		145.8	106.6				100.9	60.4		
4		76.2	129.0	121.0	27.7	27.7				
5		76.2	129.0	121.0	27.6	27.6	100.9			
6								55.3		
7	27.2	122.8	130.8	25.2	17.3		100.8			
8							101.1	56.0	168.7	20.8
9		143.2	106.5					55.7		24.9
10							101.0	55.4		

SFORD spectra C-3′ and C-4′ show second-order features whereas C-1 gives a simple doublet. Differentiation of C-3′ and C-4′ comes from consideration of the related compounds morellin,[12] β-toxicarol,[13] and elongatin[14] all of which have the 2,2-dimethyl chromene system but have a hydroxy group at C-1. The first two compounds both show signals[12,16] at 126 and 115 ppm (in $CDCl_3$) which in the case of morellin have been assigned to C-3′ and C-4′ respectively. These assignments are confirmed[17] by the second-order aspect of the SFORD signals in elongatin (129 and 114 ppm in DMSO-d_6) and the fact that the lower field signal is, in the ^{1}H-coupled spectrum the more coupled, presumably to the 2,2-dimethyl protons. Reasonably, therefore, in **4** and **5** C-3′ resonates at the same field as in elongatin but C-4′ at 7 ppm higher field than its counterpart.

Quaternary carbons. These fall in the range 133–160 ppm when bonded to oxygen and in the range 110–121 ppm when not bonded to oxygen. Division into A- or D-ring carbons is again obvious since change in the substitution of one ring has no effect on the chemical shifts of the other. Assignments for the D-ring are straightforward since only C-7a is not bonded to oxygen and in the compounds with a bridging methylene dioxy group the order C-10a > C-9 > C-8 is expected from the oxidation pattern and supported by the position of the signals in compound **10**. The methylation shifts shown by comparison of **4** with **1** and **6** give unambiguous D-ring assignments in these compounds. Of the A-ring carbons, C-4 in **3** is at uniquely high field since it is flanked by two oxygen functions but frequently distinction between C-1a and C-2 and between C-3 and C-4a cannot be made from the pterocarpan chemical shift data. The ^{1}H-coupled spectra (Fig. 2) show that in **4** and **5** one of the pair C-1a, C-2 is more coupled than the other. Although both these carbons could show two ^3J(C,H) and two ^2J(C,H) the coupling ^3J(C-1a, H-6a) is expected to be small because of the dihedral angle required from the conformation of the coumaranochroman system so that the least coupled of the pair is assigned to C-1a. The ^{1}H-coupled spectrum of **7** also shows the resonance assigned to C-1a as the less coupled. In compound **9** inspection of the $Yb(fod)_3$ induced shifts ($CDCl_3$ solution) gave the assignments since complexation can be expected to be predominantly at the hydroxy function. The data for **9** together with the chemical shifts (121.2 ppm) reported for the carbon analogous to C-2 in 6-methoxy benzofuran[18] indicate the assignments for C-1a and C-2 in compounds **1**, **2** and **3**. C-3 and C-4a are at very similar field positions and therefore difficult to distinguish, but in all the pterocarpans (excepting **3** and **6** which have different A-ring substitution pattern) a constant resonance is observed at 153.6 ± 0.4 ppm which is assigned to C-4a.

CONCLUSION

These ^{13}C results should complement ^{1}H data in the characterisation of new related compounds, and perhaps make degradative procedures unnecessary. The most useful feature is the complete independence of the A- and D-ring chemical shifts. The C-6, C-6a and C-11a resonances are also largely independent of A- and D-ring substitution. New compounds substituted on these carbons or with different B/C ring junction stereochemistry will show changes in these easily assigned resonances.

EXPERIMENTAL

Spectra were recorded at 20 MHz using a Varian CFT-20 spectrometer equipped with 16 K computer. Samples (0.1–1.0 M) in DMSO-d_6 were contained in 10 mm sample tubes and were run at 60°C to aid solution. All spectral widths were 4000 Hz and free induction decays were accumulated with 2 data points/Hz using 90° pulses and pulse delays of 0–5 sec. Chemical shifts were referenced to the centre solvent line and corrected (+39.6 ppm) to TMS. Gated decoupling was used for the ^{1}H-coupled spectra.

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