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^{13}C NMR AND CD OF SOME 3,8″-BIFLAVANOIDS FROM *GARCINIA* SPECIES AND OF RELATED FLAVANONES

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Key Word Index—*Garcinia*; Guttiferae; biflavanoides; 3, 8″-biflavanoids; ^{13}C NMR, CD spectra.

Abstract—The ^{13}C NMR signals for most of the carbon atoms of some 3,8″-biflavanoids could be assigned with the help of the spectra of the corresponding monomers. The CD spectra of such compounds containing one flavanone and one chalcone chromophore can be used to determine the absolute configuration.

INTRODUCTION

A variety of plant species contain biflavanoids, e.g. the 3,8″ linked biflavanoids, isolated from *Garcinia* [1, 2] and *Allanblackia* [3] species, which are characteristic of the Guttiferae [4]. Recently a number of reports have appeared on the ^{13}C NMR of simple and substituted flavanoids and chalcones and the additivity rule has been tested for a large number of compounds [5, 6]. Very recently, Chari *et al.* [6a] discussed the ^{13}C NMR spectra of various C-C linked biflavanoids. On the basis of selective irradiation experiments these authors have also reversed the assignments for C-5 and C-9 in flavones made by Markham and Ternai [7]. We now report our own observations on the ^{13}C NMR of biflavanoids and also on their chiroptical properties.

RESULTS

^{13}C *NMR studies of biflavanoids*

The assignments of ^{13}C signals in the monomers made by the earlier workers [7, 8] were valuable in identifying the ^{13}C signals in our spectra. GB-1a (**1**) is a dimer of naringenin, and morelloflavone (**2**) is built up of naringenin and luteolin units [1, 9]. Both compounds show ^{13}C signals characteristic of naringenin unit (Tables 1 and 2); in addition to these, the signals characteristic of luteolin are also seen in the spectra of the latter.

Ring C *and* C′. The highest field signals at 43.0, 47.7, 78.3 and 81.7 ppm in the spectrum of GB-1a arise from C-2, C-2″, C-3 and C-3″ carbons of rings C and C′. From the 'off-resonance' spectrum it is evident that the signal at 43.0 ppm is due to C-3″. The next lower field signal at 47.7 ppm was assigned to C-3, and is shifted downfield due to flavanyl substitution. The signal at 78.3 ppm must be due to C-2″ and the 3-substitution has caused the downfield shift of the signal of C-2 to 81.4 ppm. Such an assignment is supported by the pattern of signals obtained for C-2 and C-3 of morelloflavone (**2**) which appear at 81.0 and 48.7 ppm, respectively. From the above result it appears that the extent of downfield shift of the C-2 and C-3 signals of ring C of the naringenin units varies slightly with different types of flavanyl substituents at C-3. C-2″ and C-3″ of ring C′ in **2** are resonating at 163.2 and 102.4 ppm, respectively. In the lowest field region the signals at 195.6 and 181.3 ppm of **2** are due to C-4 (flavanone carbonyl) and C-4″ (flavone carbonyl), respectively, and this is in good agreement with the assignments made by previous workers [7, 8]. Such distinction could, however, not be made for **1**. The two flavanone carbonyl signals appear at 196.1 and 195.2 ppm.

Rings B *and* B′. There are four intense signals at 114.5, 114.9, 128.5, and 128.9 ppm in the spectrum of **1**. These signals are split into doublets in the 'off-resonance'

Table 1. ^{13}C chemical shifts of flavanones and chalcones*†

	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
GB-1a (**1**)	81 4	47 7	195 2*	163.4	96 0	165 9	95 0*	162 3	101 3	127.9	128 5	114 5	157 1	114.5	128 5
GB-1a hexamethyl ether	82 1	48 8	197 2	164 4	95 3	167 7	94 1	163 0	103 2	130.2	128 6	113 5	159 9	113.5	128 6
Morelloflavone (**2**)	81 0	48 7	195.6	163.5	96 2	166 3	95 2	162 5	101 5	128 0	128 1	114.4	157 1	114 4	128 1
GB-1a heptamethyl ether **3**	81 7	51 0	193 7	164 6	93 3*	164 9	93 1*	162 1	105 8	130 3	128 2	113 2	159 1	113.2	128 2
GB-2a octamethyl ether **4**	81 6	51 1	193 4	164.5	93 4	165 0	93 0	162 0	105 7	130 3	128.1	113 1	159 1	113 1	128 1
	C-2″	C-3″	C-4″	C-5″	C-6″	C-7″	C-8″	C-9″	C-10″	C-1‴	C-2‴	C-3‴	C-4‴	C-5‴	C-6‴
1	78 3	43 0	196 1*	162.3	94.9*	164 3	101 3*	162.0	101 0*	128.9	127.3	114 9	157 1	114 9	127.3
1 Hexamethyl ether	79 1	46 1	189.5	164 4	89 2	167 7	102 9	162 0	106.0	130 9	127 8	114.1	159 9	114 1	127 8
2	163 2	102 4	181 4	160 3	98 6	161 4	100 5	155.0	103.2	121 2	113.1	145 4	149.4	116 1	119 0
3	144 4	126 4	189 3	157 5	91 5	159 0	115 4	157 1	110.5	127 2	129 7	113 9	161 0	113 9	129 7
4	144 6	126 6	189 2	157 3	91 6	159 1	115 4	157 1	110 5	127 3	109 9*	148 8	150 9	110 9*	122 8

* Solvent: $CDCl_3$ for all substances except for naringenin (DMSO-d_6). Chemical shifts marked by an asterisk may be interchanged pairwise.

† For sake of comparison the chalcone atoms are numbered in the same manner as for flavanones in the table.

Table 2. ^{13}C chemical shifts of biflavanoids and their methyl ethers†

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
Naringenin	78.4	42.0	196.1	163.5	95.9	166.7	95.1	162.9	101.8	128.9	128.2	115.2	157.8	115.2	128.2
Naringenin-7,4′-dimethyl ether	79.0	43.2	196.0	164.2	95.1	168.0	94.2	162.9	103.2	130.6	127.7	114.3	160.1	114.3	127.7
Naringenin trimethyl ether	79.0	45.5	189.2	165.1	93.7	166.0	93.2	162.4	106.1	131.0	127.7	114.2	160.0	114.2	127.7
2′-Hydroxy-4,4′,6′-trimethoxy chalcone†	142.4	125.3	192.6	162.6	93.9	168.5	91.3	166.1	106.5	128.5	130.1	114.4	161.5	114.4	130.1
2′,4,4′,6′-Tetramethxoychalcone†	143.8	127.1	193.8	158.8	91.0	162.4	91.0	158.8	112.2	127.7	130.0	114.4	161.5	114.4	130.0
3′-Methyl-2′,4,4′,6′-tetra-methoxychalcone†‡	144.5	127.1	194.6	157.4	91.7	160.2	117.0	156.3	112.3	127.8	130.2	114.4	161.6	114.4	130.2

† Solvent: DMSO-d_6 for hydroxy compounds; $CDCl_3$ for methyl ethers. Chemical shifts marked by an asterisk may be interchanged pairwise.

‡ $\delta(C{-}CH_3) = 8.5$ ppm.

spectrum and must be due to the C-2′/C-6′, C-3′/C-5′, C-2‴/C-6‴, and C-3‴/C-5‴ carbons of rings B and B′. The C-2′/C-6′ and C-3′/C-5′ carbon signals of the unsubstituted naringenin appear at 128.2 and 115.2 ppm, respectively. Hence it follows that in **1** the upfield signals must be due to C-3′/C-5′, C-3‴/C-5‴, and the downfield signals due to C-2′/C-6′, C-2‴/C-6‴. In **2** the signals due to C-2′/C-6′ and C-3′/C-5′ of ring B have been located at 128.1 and 114.4 ppm. There is a good correspondence of these signals with those at 128.5 and 114.5 ppm in **1** suggesting the possibility of the latter signals representing the C-2′/C-6′ and C-3′/C-5′ carbons, respectively, of ring B in **1**. On comparison with the spectrum of luteolin [7] the C-2‴, C-5‴, and C-6‴ carbon signals of ring B′ in **2** were located at 113.1, 116.1 and 119.0 ppm, respectively.

There is no difficulty in identifying the signals due to C-1′ and C-1‴ in **1**, which appear at 127.9 and 128.9 ppm and again the upfield shift of the signals of C-1′ by 1.0 ppm can be attributed to the C-3 substitution. The C-1′ signal in **2** appears at 128.0 ppm and the signal at 121.2 ppm we assigned to C-1‴. An intense signal at 157.1 ppm in the spectrum of **1** represents both the C-4′ and C-4‴ carbons. In the spectrum of **2** C-4′ has the same chemical shift of 157.1 ppm, and C-3‴ and C-4‴ resonate at 145.4 and 149.4 ppm, respectively.

Rings A and A′. Among the ring A and A′ carbons the signals of C-6, C-8 and C-6″ are expected to be in the highfield region of the spectrum. In naringenin the C-6 and C-8 carbons resonate at 95.9 and 95.1 ppm, respectively. GB-1a (**1**) shows three signals at 96.0, 95.0 and 94.9 ppm, representing methine carbons. The downfield signal at 96.0 ppm must belong to C-6; the other two signals due to C-8 and C-6″ are, however, in so close proximity to each other, that it is impossible to differentiate between the two on the basis of this evidence. The naringenin unit in **2** shows signals at 96.2 and 95.2 ppm due to C-6 and C-8 carbons, respectively. The chemical shifts for the C-6 carbon of unsubstituted luteolin [7] has been quoted as 99.2 ppm, which is now expected to be shifted upfield by the C-8″ substitution in **2**; in fact it is shifted by about 0.6 ppm and appears at 98.6 ppm.

By similar comparison with naringenin and luteolin, the signals at 101.3 and 101.0 ppm have been assigned to C-10 and C-10″ in **1**, and the signals at 101.5 and 103.2 ppm to C-10 and C-10″, respectively, in **2**.

The spectrum of GB-1a (**1**) shows six lines in the region 166 to 157 ppm due to eight oxygenated carbons. Amongst these the one at 157.1 ppm has been shown to correspond to C-4 and C-4‴ carbons (*vide supra*). The remaining five lines should represent six carbons. Similarly, the spectrum of morelloflavone (**2**) shows ten lines in the 166 to 145 ppm region due to nine oxygenated carbons and the C-2″ carbon. Four lines have already been accounted for C-2″, C-4′, C-3″ and C-4″ carbons (*vide supra*). The unaccounted six lines represent six oxygenated carbons which are obviously C-5, C-5″, C-7, C-7″, C-9, C-9″.

A ^{13}C NMR study of 5,7-oxygenated flavones [5, 8, 10, 11] shows that among the C-5, C-7 and C-9 carbons the C-7 signal always appears at lowest field. Taking this observation into consideration, we assigned the lowfield signals at 165.9 and 164.3 ppm to C-7 and C-7″ in **1**. It appears that the substitution at C-8″ caused the upfield shift of C-7″ signal by *ca* 1.6 ppm. It is expected that the C-9″ carbon signal also should be shifted upfield and hence the signal at 162.0 ppm has been assigned to that carbon. The signal at 163.4 ppm must be due to C-5, while that at 162.3 ppm is very intense and thus represents C-5″ and C-9.

In the spectrum of **2** the lowfield signal at 166.3 ppm has been assigned to C-7 and the corresponding signals for C-5 and C-9 from the naringenin part in **2** appear at 163.5 and 162.5 ppm. Amongst the three unassigned signals at 161.4, 160.3, and 155.0 ppm, the lowfield signal should belong to the C-7″ carbon. Here it should be pointed out that the assignments made by Ternai and Markham [7] for C-5 and C-9 in quercetin have been reversed by Lallamand and Duteil [11] on the basis of an undecoupled spectrum. If this applies to luteolin, we assume that among the two signals at 160.3 and 155.0 ppm the latter belongs to C-9″ and the former to C-5″. The comparison of the intensities of these two signals shows that the signal at 155.0 ppm is far less intense, and in fact such behaviour is expected for the C-9″ signal caused by the lack of the nuclear Overhauser effect due to the absence of protons in the vicinity [12].

The only unaccounted signal at 100.5 ppm in the spectrum of **2** we assign to C-8″. The spectrum of **1** shows an intense signal at 101.3 ppm which has been assigned to C-10 (see above), however, taking into consideration its intensity, we assume that C-8″ signal coincides with it. The possibility of the signal at 101.3 ppm accounting for both C-10 and C-10″ and the signal at 101.0 ppm representing C-8″ cannot be ruled out. The total assignment of the carbon signals in the spectrum of GB-1a hexamethyl ether has been made in comparison with model compounds (Table 1) and GB-1a (**1**) (see Table 2).

^{13}C *NMR studies of flavanone-chalcones*

These compounds were obtained by the methylation of the corresponding biflavanoids using dimethylsulphoxide and anhydrous potassium carbonate in boiling

Table 3. ^{13}C chemical shifts of the methoxy carbons

Substance	OCH_3 groups attached to							
	C-4′	C-4‴	C-5	C-5″	C-7	C-7″	C-9	C-9″
Naringenin 7,4′-dimethyl ether	55.3	—	—	—	55 6	—	—	—
Naringenin trimethyl ether	55.3	—	56.1	—	55 6	—	—	—
GB-1a hexamethyl ether	55.4	55.4	56.1	56.1	55.7	55.9	—	—
3	55.0, 55.2, 55.3, 55.7, 55.8, and 56.0; no individual assignment possible						—	62.5
4	54.9, 55.3, and 55.7 (corresponds to 4 signals); no individual assignment possible						—	62.4
2′-OH-4,4′,6′-TriOMe chalcone	55.4	—	—	—	55.5	—	55.8	—
2′,4,4′,6′-TetraOMe chalcone	55.2	—	55.8	—	55.2	—	55.8	—
3′-Me-2′,4,4′,6′-tetra OMe chalcone	55.4	—	55.8	—	56.2	—	62.1	—

acetone. The ^{13}C NMR spectrum of GB-1a heptamethyl ether (**3**) shows 28 signals and that of octamethyl ether (**4**) 31 lines.

The signals corresponding to C-2 and C-3 appear at 81.7 and 51.0 ppm in **3**, and 81.6 and 51.1 ppm in **4**. The lowest field signal at 193.7 ppm in **3** must be due to C-4 (flavanone carbonyl) and is shifted upfield by about 2 ppm due to absence of hydrogen bonding. The C-4″ (chalcone carbonyl) signal appears at 189.3 ppm. The corresponding signals of **4** are observed at 193.4 and 189.2 ppm.

The carbon signals in the rings B and B′ of **3** and **4** were assigned analogously to those of **1** and **2**. However, the signals corresponding to C-2‴ and C-5‴ in **4** could not be assigned safely and may be interchanged.

The C-6, C-6″, and C-8 signals of **3** appear at 93.3, 93.1, and 91.5 ppm. Among these the C-6″ carbon signal is expected to be shifted upfield due to C-8″ substitution, hence the upfield signal at 91.5 ppm was attributed to C-6″, but a distinction between the signals due to C-6 and C-8 could not be made. There is a very good correspondence between the signals due to the carbons of the flavanone part of **3** and **4** and almost identical chemical shifts are observed for the corresponding carbons (Table 2). The methylation shifts are almost negligible. Considerable influence on the carbons of ring A′ has occurred due to the ring opening. The C-7″ signal now appears at 159.0 ppm and those of C-5″ and C-9″ at 157.5 and 157.1 ppm in **3**.

Methoxyl carbons. All methoxyl signals (Table 3) appear in the range of about 55 to 56 ppm with two exceptions (62.5 and 62.4 ppm). It is known from the literature [13] that in *ortho*-disubstituted anisoles the methoxyl carbon signals are shifted downfield considerably compared with anisole itself. This led us to the conclusion that the 62.5 and 62.4 ppm signals have to be assigned to the C-9″ methoxyl carbons of **3** and **4**, respectively. The spectra of the three model chalcones (2′-hydroxy-4,4′,6′-trimethoxy,2′,4,4′,6′-tetramethoxy, 3′-methyl-2′,4,4′,6′-tetramethoxy) support this assignment.

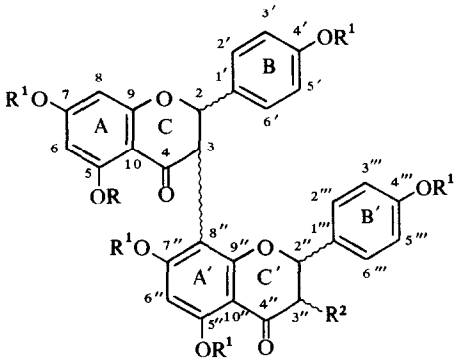
These results reveal that two *ortho* substituents may cause a considerable downfield shift of a methoxyl carbon signal due to steric crowding. Furthermore, the cinnamyl group seems to increase the downfield effect compared with a methyl group, since the signal of the methoxyl carbon of 2,6-dimethylanisole appears at 59.4 ppm.

In the ^{1}H NMR spectra of **3** and **4** the proton signals of this particular methoxyl group are shifted upfield by about 0.3 to 0.5 ppm. Since this shielding effect does not exist in the ^{1}H NMR spectrum of 3′-methyl-2′,4,4′,6′-tetramethoxychalcone, it may be attributed rather to an

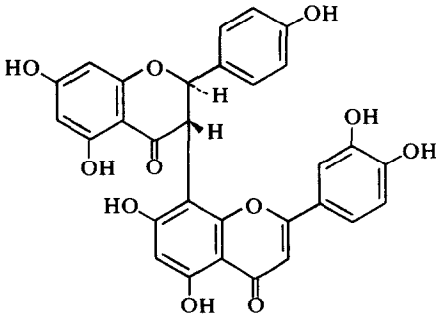
Table 4

Substances	CD maxima given as λ_{max} (in nm), Δε-values in parentheses; solvent is ethanol								
Dihydrokaempferol	330 (+1.23)	292 (−4.65)	255 (+0.80)	234 (+1.36)	215 (+5.00)				
(+)-Taxifolin	369sh (+0.11)	332 (+2.86)	296 (−10.45)	252 (+1.64)	221 (+9.23)	206 (−5.33)			
Dihydromorin	358sh (+0.09)	328 (+0.52)	295 (−1.74)	257 (+0.31)	231sh (+0.70)	221 (+1.23)			
GB-1a	343 (+1.42)	319sh (−0.43)	305sh (−3.20)	297 (−4.51)	278 (+5.76)	245 (−2.16)	233 (+2.86)	211 (−14 45)	197 (−25.38)
GB-1	340 (+1.72)	305 (−6.87)	298sh (−4.50)	280 (+8.68)	246 (−1.90)	236 (+2.38)	222sh (−8.00)	212 (−13.13)	
Morelloflavone	350 (+2.22)	294sh (+4 80)	287 (+5.75)	263sh (−1.00)	227 (−10.46)	213 (−8.42)			
GB-1a hexamethyl ether	366 (+0.56)	328 (−7.64)	305sh (+2.00)	281 (+10.68)	241 (−7.48)	239 (−7.46)	213 (−26.74)	197 (−16.12)	
GB-2a octamethyl ether	366 (+0.20)	329 (−7.50)	305sh (+3.00)	282 (+11.60)	241 (−8.70)	212 (−30.08)	197 (−19.84)		

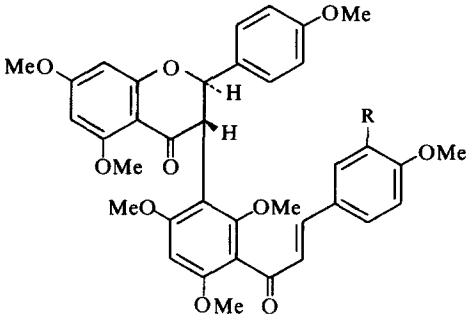
* The CD spectra of dihydrokaempferol and taxifolin have been measured before [14, 15], they are, however, included because the bands at shortest wavelength have not been recorded earlier.



1 GB-1a $R^1 = R^2 = H$
5 GB-1 $R^1 = H; R^2 = OH$



2 Morelloflavone



3 GB-1a heptamethyl ether R = H
4 GB-2a octamethyl ether R = OMe

anisotropic field effect of the carbonyl of the second flavanone unit in **3** and **4** than to the steric crowding around this methoxyl group.

CHIROPTICAL DATA OF BIFLAVANOIDS

Chiroptical data of a few biflavanoids of this type have been mentioned in the literature [1, 4], but as the order of magnitude for their g-values is quite small ($\sim 10^{-4}$), no good spectra could be obtained with older equipment. The CD spectra of monomeric flavanones have, however, been investigated more thoroughly (e.g. refs. [14–19]), and at least 4 Cotton effects can in general be observed. The empirical rule has been put forward [15] that (2*S*,3*R*)-configuration leads to a sign pattern + − + + long to short wavelengths), but for flavanones of same absolute configuration lacking the 3-substituent occasionally a sign pattern + − + − has also been found. The phenyl ring connected to C-2 always adopts equatorial conformation [20, 21] and determines thus the conformation of the dihydropyranone ring. This has even been proved for the biflavanoids [1]

Any coupling between the transition moments localized in the two aromatic rings of a flavanone is, therefore, negligible. The Cotton effect around 340 nm has been ascribed to the $n \rightarrow \pi^*$ transition of the carbonyl group [15, 22] and its sign corresponds in each case to the one predicted for such a 'tetralone' type chromophore [15, 22]. The 'conjugation band' is expected to appear between 250 and 290 nm, depending on the substitution pattern of ring A [23] and it was sometimes called just $\pi \rightarrow \pi^*$ band [15], although the other bands in the accessible range correspond also to $\pi \rightarrow \pi^*$ transitions. From the CD spectrum of dihydromorin [24, 25] the absolute configuration follows as for (2*S*, 3*R*).

The B_{2u}-Cotton effect is in general quite small and could be detected only in favourable cases. Its position in the spectrum can approximately be predicted [26] and this helps to identify the CD band (Table 4).

In the dimers **3** and **4** only the flavanone moiety is chiral, and the 'chalcone-substituent' is again equatorially arranged, as follows from the coupling constant $J_{2,3} = 12$ Hz. Any coupling mechanism could thus again be operating only for very strong electric transition moments, i.e. only for high energy transitions. The achiral chalcone unit is chirally perturbed by the 'flavanone-substituent', but for this extended chromophore (achiral first and second sphere) relatively small $\Delta\varepsilon$-values can be expected. Those measured by us (Table 4) are much too strong for this, and so we can safely assume that the CD bands (at least above 230 nm) come mainly from the flavanone chromophore (chiral first and/or second sphere). A comparison of the CD spectra of **3** and **4** with e.g. that of taxifolin [14] or (−)-naringenin glucoside [16] between 400 and 210 nm clearly shows that the absolute configuration must be (2*R*, 3*S*) for both compounds.

In morelloflavone (**2**) the flavone moiety is also achiral but due to ring closure not flexible. The chiral perturbation from the 'flavanone-substituent' is thus much stronger, and indeed flavone *C*- and *O*-glycosides may also give Cotton effects of considerable magnitude and comparable to those of the flavanones [25–27]. The absolute configuration of the latter moiety must be the same as for **3** and **4** because these three optically active compounds have been chemically correlated with each other. Furthermore, the conformation of the dihydropyrone ring is the same for these molecules, as is seen from the ^{1}H NMR spectra. A comparison of the CD spectra of **2** with that of **4** shows that the 'conjugation band' CD still remains mainly unchanged, the negative Cotton effect around 330 nm of **4** is, however, overcompensated by a positive one centred around 350 nm in the CD spectrum of **2**. This is the wavelength range where optically active flavones show their first Cotton effect [27–29]. Obviously the 'flavone-substituent' perturbs the flavanone $n \rightarrow \pi^*$ transition much more than the very flexible chalcone moiety.

The two dimers **1** and **5** show nearly identical CD spectra over the entire wavelength range, so they must have the same configuration at all those chiral centres common to them. On the basis of the arguments men-

tioned for the CD of **2** a prediction of the absolute configuration from the CD spectra is not reliable.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded with a Bruker WH-90 spectrometer operating at 22.64 MHz in the FT mode, the solvent was DMSO-d_6 for the hydroxylated compounds, $CDCl_3$ for the methyl ethers. The chemical shifts are referred to internal TMS, positive values correspond to downfield shifts. The CD spectra were recorded with the dichrograph Mark III (Jobin-Yvon) connected on-line to a PDP-8 computer at room temp. in cells of 0.01 to 2.00 cm length and at concentrations of *ca.* 1 mg/cm^3.

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