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PROPERTIES OF SOME METHYLELLAGIC ACIDS AND THEIR GLYCOSIDES

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Key Word Index—*Eucalyptus*; Myrtaceae; methylellagic acid and derivatives; ellagic acid; spectral and chromatographic properties; chemotaxonomy.

Abstract—Methylellagic acids and their glycosides have been isolated from or detected in different tissues of eucalypts. These compounds appear to constitute a taxonomic character and to facilitate their detection a number of their properties are reported.

INTRODUCTION

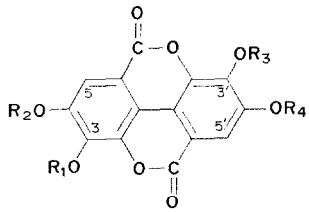
ELLAGIC acid is found in the leaves, bark, wood, petals and wound exudates of certain orders of the dicotyledons.[1] It is frequently accompanied by esterified hexahydroxydiphenic acid 'ellagitannins' which also have taxonomic importance.[2] These substances can cause difficulties in the pulping of wood and during paper making[3] and also the ellagitannins are fungitoxic.[4]

The methylellagic acids and their glycosides have rarely been reported, possibly owing to the difficulties in their isolation, purification and identification. Some of them are particularly insoluble to an extent which limits their characterization by chromatographic and spectral techniques. Furthermore they may be included in the lignins isolated from woods containing them and thus affect the composition of the lignins. They have been reported in a number of eucalypt woods[5] but their influence on commercial operations is not yet known.

A recent study[6] of the distribution of 3-*O*-methylellagic acid, 3,3′-di-*O*- and 3,3′,4-tri-*O*-methylellagic acids in the bark, wood and stems of members of Hutchinson's order Myrtales has shown their value as taxonomic characters. Some chromatographic methods for detection[6,7] have been reported for the above compounds. In the course of our studies we have isolated additional derivatives including glycosides and if the anthocyanins be taken as a guide the patterns of the glycosidic combinations may be of more taxonomic interest than the distribution of the aglycones.[8] Some of the methylellagic acids can be confused chromatographically with hydroxystilbenes with which they sometimes co-occur. The unknown compounds *A* and *B* reported in the taxonomic survey of the acid hydrolysed products of some eucalypt species[9] appear to be methylellagic acids. Although there was little relationship

[1] BATE-SMITH, E. C. (1956) *Chem. Ind.* B.I.F. Rev., R32.
[2] BATE-SMITH, E. C. (1972) *Phytochemistry* **11**, 1755.
[3] HILLIS, W. E. (1972) *Phytochemistry* **11**, 1207.
[4] HART, J. H. and HILLIS, W. E. (1972) *Phytopathology* **62**, 620.
[5] HILLIS, W. E. (1972) *Appita* **26**, 113.
[6] LOWRY, J. B. (1968) *Phytochemistry* **7**, 1803.
[7] CAIN, B. F. (1962) *N.Z. J. Sci.* **5**, 390.
[8] HARBORNE, J. B. (1963) in *Chemical Plant Taxonomy* (SWAIN, T., ed.), Academic Press, London.
[9] HILLIS, W. E. (1966) *Phytochemistry* **5**, 1075; (1967) **6**, 259; (1967) **6**, 275; (1967) **6**, 373; (1967) **6**, 845.

between observed distribution and taxonomic affinities, this may be due to inadequacies of the chromatographic methods used at that time. We present this summary of different properties of a number of these compounds to assist their identification, detection and the prediction of the constitution of new members of the class. The data should also assist the assessment of their taxonomic significance and influence in commercial processes.



(I) R_1, R_2, R_3, R_4 = Me
(II) R_1, R_2, R_3 = Me; R_4 = H
(III) R_1, R_2, R_3 = Me; R_4 = Glc
(IV) R_2, R_4 = Me; R_1, R_3 = H
(V) R_1, R_3 = Me; R_2, R_4 = H
(VI) R_1, R_3 = Me; R_4 = Glc; R_2 = H
(VII) R_1 = Me; R_2, R_3, R_4 = H
(VIII) R_1 = Me; R_4 = Rha; R_2, R_3 = H
(IX) R_1, R_2, R_3, R_4 = H

SCHEME 1. METHYLELLAGIC ACID DERIVATIVES.

RESULTS AND DISCUSSION

Methylellagic acids and their derivatives are readily detected on paper chromatograms by their mauve fluorescence in UV light (254 nm). The intensity of fluorescence per unit weight of the compounds varies but the colour is similar to that of ellagic acid although some weakly mauve components become pink when the chromatogram is dried; in most cases the compound becomes yellow rapidly in ammonia vapour (Table 1). This colour change enables distinction from hydroxystilbenes which in some cases have similar R_f values.

TABLE 1. CHROMATOGRAPHIC DATA OF ELLAGIC ACID, METHYLELLAGIC ACIDS AND DERIVATIVES

Compound	PC* R_f (100) BAW	HOAc	For.	BEN	TLC† R_f (100) MCP	ECF	BAD	Colour on paper under UV (254 nm) UV	UV/NH_4OH
I (3,3′,4,4′-tetra-Me)	87	10	96	74	60	83	85	Blue	Blue
II (3,3′,4-tri-Me)	82	6	91	42	39	52	64	Mauve	Yellow
III (3,3′,4-tri-Me 4′-gluc)	57	41	93	77‡	0	0	0	Blue	Blue
V (3,3′-di-Me)	76	4	84	7	31	32	55	Mauve	Yellow
VI (3,3′-di-Me 4′-gluc)	50	30	91	8	0	0	0	Mauve	Yellow
VII (3-Me)	58	3	62	3	0	16	33	Weak mauve	Greenish yellow
VIII (3-Me 4′-rham)	53	15	84	1	0	0	0	Weak mauve	Greenish yellow
IX (Ellagic)	38	2	34	0	0	0	0	Mauve	Yellow

* On Whatman No. 1 paper using BAW (*n*-BuOH–HOAc–H_2O, 6:1:2), 6% HOAc, For. (Forestal, HCl–HOAc–H_2O, 3:30:10), BEN (*n*-BuOH–EtOH–1·5 N NH_4OH, 4:1:3 top phase).

† TLC on silica gel GF 254 at a thickness of 250 μ using MCP (MeOH–$CHCl_3$–petrol (b.p. 100–120°), 2:4:7), ECF (EtOAc–$CHCl_3$–HCOOH, 2:10:1), BAD (C_6H_6–HOAc–dioxan, 90:4:25).

‡ Streak.

The chromatographic data using both PC and TLC (Table 1) facilitate the identification of the compounds. When the number of free hydroxyls is 2 (and usually 3) or less there is a linear relationship between these and the R_f values (PC), with the exception of the glycosides in BAW. With Forestal solvent the type of substituent had no effect on R_f value, and with 6% HOAc the decrease is more abrupt with the glycosides but the R_f values are higher than with the aglycones. With BAW the presence of rhamnose results in a R_f value higher than that expected. BAW and BEN are the best PC solvents for aglycones and 6% HOAc for glycosides. TLC examination showed the same steady increase in R_f values with decrease in free hydroxyl groups and the solvent ECF was the most useful.

TABLE 2. UV SPECTRA OF ELLAGIC ACID, METHYLELLAGIC ACIDS AND DERIVATIVES

Compound‡	λ_{max} (nm)† MeOH	MeOH + AcONa	MeOH + NaOEt‡	MeOH + $AlCl_3$
II (3,4,3′-Tri-Me)	247 (1·76)§	253 (1·30)	255 (1·60)	
	287 (0·40)‖	279 (1·01)‖	276 (1·40)‖	
	356 (0·42)‖			
	370 (0·46)	408 (0·38)	404 (0·49)	
II Mono-acetate	246 (1·35)	246 (1·44)	249 (1·11)	
	287 (0·50)‖	287 (0·50)‖	282 (0·74)‖	
	343 (0·26)‖	343 (0·27)‖	358 (0·20)	
	359 (0·30)	359 (0·31)	400 (0·19)	
III (3,4,3′-Tri-Me 4′-gluc)	247 (1·50)	247 (1·50)	247 (1·70)	
	287 (0·40)‖	287 (0·45)‖	287 (0·56)‖	
	350 (0·35)‖	350 (0·35)‖	350 (0·34)	
	367 (0·40)	367 (0·40)	367 (0·38)	
V (3,3′-Di-Me)	247 (1·38)	256 (1·14)	246 (1·12)‖	247 (1·45)
	288 (0·35)‖	310 (0·35)‖	272 (1·54)	288 (0·34)‖
	356 (0·33)‖		313 (0·56)‖	356 (0·24)‖
	374 (0·40)	409 (0·30)	426 (0·41)	374 (0·29)
VI (3,3′-di-Me 4′-gluc)	247 (1·50)	250 (1·12)	250 (1·62)	
	287 (0·32)‖	280 (0·80)‖	276 (1·41)	
	354 (0·34)‖			
	368 (0·38)	403 (0·28)	400 (0·50)	
VI Penta acetate	246 (1·66)	246 (1·66)	247 (0·91)	
	282 (0·35)‖	282 (0·40)‖	277 (0·73)‖	
	339 (0·32)	339 (0·32)		
	354 (0·36)	354 (0·36)	398 (0·22)	
VII (3-Me)	252 (1·70)	256 (1·59)	271 (1·65)	240 (0·87)
		273 (1·65)	291 (1·1)‖	262 (1·37)
	358 (0·38)	363 (0·51)		
	370 (0·40)		394 (0·38)	378 (0·23)
VIII (3-Me 4′-rham)	252 (1·58)	256 (1·37)		250 (1·37)
		273 (1·37)	270 (1·42)	
			292 (0·99)‖	
	350 (0·36)‖	353 (0·45)		349 (0·27)‖
	364 (0·37)		386 (0·35)	363 (0·30)
VIII Penta acetate	241 (1·67)	241 (1·77)	250 (1·54)	
	281 (0·34)‖	281 (0·49)	270 (1·34)‖	
	341 (0·38)	341 (0·41)		
	357 (0·42)	357 (0·44)	394 (0·26)	
XI (Ellagic)	255 (1·64)	254 (1·32)	254 (1·55)	247 (0·73)
		277 (1·68)	277 (1·98)	271 (1·37)
	354 (0·36)‖	357 (0·53)	355 (0·58)	
	368 (0·39)	370 (0·46)‖	370 (0·50)‖	387 (0·20)
3,3′-Deoxyellagic acid[11]	230 (1·49)	254 (1·00)‖	241 (1·17)	2·30 (1·49)
	245 (1·33)	289 (0·51)‖	263 (1·26)	2·45 (1·33)
	277 (0·48)‖	302 (0·50)	297 (0·70)‖	277 (0·48)‖
	283 (0·53)	395 (0·31)‖	310 (0·87)	283 (0·53)
	373 (0·45)‖	418 (0·34)	435 (0·47)	373 (0·45)‖
	388 (0·48)			388 (0·48)

* Tetra-*O*-methylellagic acid, 4,4′-di-*O*-methylellagic acid and 3-mono-*O*-methylellagic acid triacetate were insoluble in MeOH.

† Measured with Unicam SP 800 UV Spectrophotometer.

‡ 0·06 ml of 0·1 M NaOEt to 4 ml MeOH soln.

§ Figures in brackets represent relative absorbance at maxima in each individual spectrum; not to be compared between spectra.

‖ Shoulder.

The UV spectra of some derivatives are diagnostically useful (see also Ref. 10). The values given in Table 2 match those previously reported for 3,3′-dimethylellagic acid[10] and 3,4,3′-trimethylellagic acid.[11] The small differences between those reported in this present work for the former compound and those in an earlier study[12] are attributed to the current use of a more sensitive instrument.

In those compounds containing a free 3-hydroxyl group the addition of sodium acetate causes the appearance of a new band, in addition to the main one (at about 250 nm), and a bathochromic shift of 21–23 nm. At the same time there is a decrease in intensity of the first band (Table 2). The band at 250 nm in compounds containing free 4-hydroxyl groups is not split by the addition of sodium acetate but can be moved bathochromically. However, the use of stronger alkali can cause larger bathochromic shifts (about 60 nm) in the long wavelength band of 3,3′-di-*O*-methylellagic acid (Table 2, see also Ref. 10).

TABLE 3. IR BANDS IN ELLAGIC ACID, METHYLELLAGIC ACIDS AND DERIVATIVES*

Compound	Bands†
I (3,4,3′,4′-tetra-Me)	2950w, 2850w, 1735s, 1610s, 1570w, 1490m, 1465w, 1450w, 1445w, 1435w, 1400s, 1360s, 1350s, 1320m, 1250m, 1205w, 1165m, 1105s, 995m, 905m, 870m, 785w, 765w, 755m, 740w, 660w, 615w, 570w, 530w.
II (3,4,3′-tri-Me)	3430s, 2960w, 2850w, 1750s, 1610s, 1575w, 1490s, 1465m, 1450m, 1435m, 1410m, 1360s, 1300m, 1245m, 1200m, 1170m, 1115s, 1090s, 1060w, 990w, 915w, 860w, 780w, 755m, 740w, 610w, 575w, 530w.
III (3,4,3′-tri-Me 4′-gluc)	3430s, 2930w, 2860w, 1750s, 1610s, 1570w, 1485s, 1460w, 1450w, 1440w, 1410m, 1355s, 1325m, 1255m, 1200w, 1170w, 1150w, 1100s, 1080s, 1035m, 990m, 915w, 890w, 870w, 790w, 755w, 740w, 680w, **610w, 570w, 530w.**
IV (4,4′-di-Me)	3370m, 3100w, 2750w, 2860w, 1720s, 1620m, 1570m, 1500m, 1440w, 1430w, 1375m, 1340s, 1275w, 1225w, 1205m, 1175m, 1115m, 1085s, 960w, 910w, 870w, 820w, 755m, 740w, 660w, 575w, 550w, 530w.
V (3,3′-di-Me)	3400m, 2960w, 2850w, 1725s, 1610s, 1580m, 1485s, 1440m, 1355s, 1285m, 1215s, 1175m, 1105s, 1070m, 990m, 915w, 870w, 795w, 760w, 740w, 625w, 575w, 535w.
VI (3,3′-di-Me 4′-gluc)	3430m, 3340m, 2920m, 2850w, 1750s, 1725s, 1610m, 1575w, 1480m, 1440w, 1415w, 1390w, 1355s, 1325w, 1305w, 1275w, 1240m, 1195w, 1170m, 1145m, 1125m, 1105s, 1075s, 1030s, 1010m, 980m, 910m, 895w, 870w, 790w, 755m, 730w, 665w, 630w, 570w, 530w.
VII (3-mono-Me)	3420s, 2960m, 2840m, 1715s, 1600s, 1585s, 1495s, 1425s, 1360s, 1340s, 1325s, 1285m, 1190s, 1110s, 1060s, 970w, 915m, 870w, 795w, 755m, 685w, 630w, 605w, 570w, 520w.
VIII (3-mono-Me 4′-rham)	3420s, 2960w, 2840w, 1730s, 1600s, 1570m, 1490s, 1430m, 1345s, 1285m, 1240m, 1205m, 1100s, 1055s, 995w, 965m, 915m, 895w, 835w, 810w, 800w, 755m, 690w, 665w, 600w, 570w, 530w.
IX (ellagic)	3470s, 3140m, 1715s, 1610s, 1580m, 1500m, 1440m, 1395m, 1365m, 1320s, 1255m, 1190m, 1105s, 1035s, 920w, 900w, 870w, 810w, 755m, 670w, 630w, 570w, 535w.

* In KBr disks using Perkin Elmer 457 Grating Infrared Spectrophotometer.
† w—weak; m—medium; s—strong intensity of bands. Values in cm^{-1}.

The IR spectra (Table 3) show some variability in the position and configuration of the peaks, presumably due to the differing degrees of hydrogen bonding present in the solid state. Absorptions are in the following regions: hydroxyl (3470–3140 cm^{-1}), –CH of methoxyl (2960–2920; 2860–2840 cm^{-1}), carbonyl (1750–1715 cm^{-1}; the carbonyl absorp-

[10] JURD, L. (1959) *J. Am. Chem. Soc.* **81**, 4610.
[11] MOORE, B. P. (1964) *Australian J. Chem.* **17**, 901.
[12] HILLIS, W. E. and INOUE, T. (1967) *Phytochemistry* **6**, 59.

tion is stabilized to a single peak at 1735 cm^{-1} in the tetra-methyl derivative), aromatic rings (1610–1600, 1585–1570, 1500–1480 cm^{-1}), C–O–C of glucose (1035–1030 cm^{-1}); β-glucose (895–890 cm^{-1}); an unidentified feature at 760–755 cm^{-1}. The values given in Table 3 are identical with those published for 3,4,3′-trimethylellagic acid[11] and those for 3,3′-dimethylellagic acid[11] are within the above region.

TABLE 4. NMR SPECTRA OF ELLAGIC ACID, METHYLELLAGIC ACIDS AND DERIVATIVES*

Compound	Aromatic hydrogens† (H)		Aromatic methoxyls† (—Me)				Glucose H-1	Rhamnose H-1	Rhamnosyl $-CH_3$
	(5)	(5′)	(3)	(3′)	(4)	(4′)			
I (3,4,3′,4′-tetra-Me)‡	7·64	7·64	4·03	4·03	3·98	3·98			
II (3,4,3′-tri-Me)	7·44	7·38	3·96	3·98	3·91				
III (3,4,3′-tri-Me 4′-gluc)	7·44	7·71	3·94	4·01	3·88		5·08 5·03		
V (3,3′-di-Me)	7·38	7·38	3·99	3·99					
VI (3,3′-di-Me 4′-gluc)	7·36	7·71	3·97	4·03			5·10 5·04		
VII (3-Me)	7·34	7·40	3·98						
VIII (3-Me 4′-rham)	7·42	7·65	4·00					5·42	1·13 1·08
IX (ellagic)	7·40	7·40							

* Spectra recorded in deuterodimethylsulphoxide on a Varian HA-100 spectrophotometer coupled with a Computer 620/L. Values are given in ppm (δ scale) relative to TMS as internal standard.

† Proposed assignments: see Fig. 1 for location of positions.

‡ The very low solubility of this compound may have affected values; 40 computer runs were required.

The NMR chemical shifts (Table 4) enable some predictions of the assignments of the aromatic protons to be made as well as some suggestions as to whether the methoxyl substituent is in the 3 or 4 position. These studies were hampered by low solubility in the solvents and with some compounds several computer runs were made to obtain satisfactory spectra. In such cases, the low solubilities may have made small differences in the value of the shifts. The assignments given in Table 4 show a higher degree of consistency with observed and expected values than other possible assignments. We postulate that in tri-*O*-methylellagic acid, the 3 and 4 methoxyl groups on the one ring have shifts of 3·96 and 3·91 ppm respectively. On the other ring, with only one methoxyl at the 3′ position the shift is 3·98 ppm. The decrease in shift for the aromatic proton adjacent to a glycoside substituent is sufficiently large for diagnosis. The data support the view that the new compound VIII is a 4′-glycoside and hydrolysis of its methylated derivative yields 3,4,3′-tri-*O*-methylellagic acid and rhamnose. Its examination is reported in more detail elsewhere.

The description of the unknown compounds *A* and *B*[9] in the hydrolysates of *Eucalyptus* leaves resemble those given for the methylellagic acids described above. The R_f values reported earlier were taken from chromatograms of the crude hydrolysates and consequently could have been affected by the presence of other materials. Fresh leaves of *E. calophylla* were hydrolysed as previously but it was found that the methylellagic acid were more effectively removed with ethyl acetate than the usual amyl alcohol. Appreciable amounts of mono-*O*-methylellagic acid and lesser amounts of di- and tri-*O*-methylellagic acids were indicated by chromatographic comparison with authentic specimens. In addition, from spectral data compound *A* was identified as 3-mono-*O*-methylellagic acid and compound *B* as 3,3′-di-*O*-methylellagic acid. Tri-*O*-methylellagic acid was also identified spectrally but this compound was not differentiated in the earlier work[9] because of the presence of other compounds in the same regions of the chromatograms. These methylellagic acids were also identified chromatographically in *E. punctata*, *E. megacornuta*, *E. occidentalis*,

E. morrissii, *E. bridgesiana*, *E. goniocalyx*, *E. preissiana*, *E. marginata*, *E. consideniana*, *E. fergusonii*, *E. camaldulensis* and *E. sieberi*. A re-examination of eucalypt leaf hydrolysate using the improved techniques described in this paper may reveal a taxonomic significance of these compounds not evident in the earlier studies.

The m.p. (above 355°) for 3,3′-di-*O*-methylellagic acid 4′-glucoside (compound VI) is greater than that previously reported (214–215°).[13] The analysis of our material, the chromatographic purity, the sharp m.p. of its acetate and its analysis, hydrolysis to 3,3-di-*O*-methylellagic acid and glucose in the expected proportions and the data reported in this paper support the view that our compounds has this identity. Aspects of this problem will be discussed elsewhere.

Moore[11] pointed out that the nasutins (3,3′-deoxyellagic acid, 3,3′-di-*O*- and 3,4,3′-tri-*O*-methylellagic acids) were found as haemolymph components in a restricted group of termites *Nasutitermes exitiosus*. The possible origins of these materials were discussed but in our view they originate from the fodder of these insects. 3,3′-Deoxyellagic acid has several properties of ellagic acid and its derivatives, and could be overlooked in woody materials but it is conceivably a product of termite metabolism of the associated dimethylellagic acid.

EXPERIMENTAL

3,4,3′,4′-Tetra-O-methylellagic acid. Ellagic acid (100 mg) was shaken with ethereal CH_2N_2 (5 ml) for 1 hr at room temp. and completely converted to the tetramethyl derivative. (The presence of MeOH slows the rate of reaction considerably.) The derivative was recrystallized from dimethylformamide m.p. 355° (decomp.) (lit. [11]355°, [14]322–324°, [15]342°). (*Anal.* Found: C, 60·5; H, 4·1; —OMe, 34·4. Calc. for $C_{18}H_{14}O_8$: C, 60·3; H, 3·9; –OMe, 34·6%).

3,4,3′-Tri-O-methylellagic acid. Isolated from *E. polyanthemos* and *E. deglupta* heartwoods.[16] It was also prepared synthetically by methylating ellagic acid with a limited amount of ethereal diazomethane, and separating the product on a silica-gel column and eluting with $CHCl_3$. The appropriate fraction was recrystallized from dimethylformamide, m.p. 294–295° (lit. [14]297–298°, [17]293–294°). (*Anal.* Found: C, 59·3; H, 3·6; $-OMe_3$, 26·3. Calc. for $C_{17}H_{12}O_8$: C, 59·3; H, 3·5; –OMe; 27·0%).

3,4,3′-Tri-O-methylellagic acid 4′-glucoside. Isolated from *E. polyanthemos* heartwood[16] m.p. 266–267°.

4,4′-Di-O-methylellagic acid. Kindly provided by Dr. B. F. Cain.

3,3′-Di-O-methylellagic acid. Obtained by the hydrolysis of the 4′-glucoside from *E. sideroxylon* heartwood[18] m.p. and m.m.p. 340–341° (lit. [11]336–338°, [10]330–331°). It was also prepared synthetically and purified using the method described for tri-*O*-methylellagic acid (above) and eluted from the column with EtOAc–$CHCl_3$–HCOOH (2:10:1).

3,3′-Di-O-methylellagic acid 4′-glucoside. From *E. sideroxylon* heartwood[18] with m.p. darkens 265°, black 355° (lit. [13]214–215°). (*Anal.* Found: C, 53·20; H, 4·05; –OMe, 11·93. Calc. for $C_{22}H_{20}O_{13}$: C, 53·65; H, 4·06; OMe, 12·60%). The acetate of the glucoside was recrystallized as needles m.p. 251–252°. (*Anal.* Found: C, 54·7; H, 4·15; OMe, 7·92; COMe, 30·0. Calc. for $C_{32}H_{30}O_{18}$: C, 54·70, H, 4·27; OMe, 8·83; COMe, 30·62%).

3-Mono-O-methylellagic acid. Obtained on hydrolysis of the rhamnoside isolated from *E. globulus* bark[19] m.p. above 360° (lit.[14] above 360°).

3-Mono-O-methylellagic acid 4′-rhamnoside. Obtained from *E. globulus* bark[19] m.p. above 360°.

Identification of unknown compounds A *and* B. *E. calophylla* leaves were heated with about 5 × their vol. of 2 N HCl at 100° for 30 min, cooled, extracted repeatedly with EtOAc which after washing with H_2O was evaporated *in vacuo*. The extract was fractionated on thick layers (0·75 mm) of silica-gel GF254 using solvent ECF (Table 1). The appropriate bands were removed, extracted with EtOAc, purified, and their R_f determined in different solvents and spectra in different media.

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[13] ROW, L. R. and SUBBA RAO, G. S. R. (1962) *Tetrahedron* **18**, 357.
[14] CAIN, B. F. (1963) *N.Z. J. Sci.* **6**, 264.
[15] TOMITA, K., MINAMI, K. and TSURUTA, K. (1966) *J. Wood Res. Soc. Japan* **12**, 183.
[16] HILLIS, W. E. and YAZAKI, Y. in preparation.
[17] BRIGGS, L. H., CAMBIE, R. C., LOWRY, J. B. and SEELYE, R. N. (1961) *J. Chem. Soc.* 642.
[18] HILLIS, W. E., HART, J. H. and YAZAKI, Y. in preparation.
[19] HILLIS, W. E. and YAZAKI, Y. in preparation.