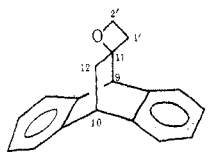
(20) Compound **13** may have been formed from a methyl vinyl ketone impurity.
(21) (a) R. Huisgen, R. Grashey, H. Seidl, and H. Hauck, *Chem. Ber.*, **101**, 2559 (1968); (b) S. S. Hall, *J. Org. Chem.*, **38**, 1738 (1973).
(22) Four batches of **7** were prepared and pyrolyzed under the above conditions. The pyrolysis of three batches was successful. Two batches were used to determine the yield of α-methyleneoxetane, which was found to be 10, 9, and 10%.
(23) (a) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **85**, 2416 (1963); (b) H. K. Hall, Jr., J. B. Dence, and D. R. Wilson, *Macromolecules*, **2**, 475 (1969).
(24) (a) S. J. Cristol and R. K. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960); (b) S. J. Cristol, J. R. Mohrig, and G. T. Tiedeman, *J. Org. Chem.*, **37**, 3239 (1972), and references cited therein.
(25) For examples of the thermal fragmentation of oxetanes, see (a) G. Jones, II, S. B. Schwartz, and M. T. Marton, *Chem. Commun.*, 374 (1973); (b) G. Jones, II, and J. C. Staires, *Tetrahedron Lett.*, 2099 (1974); (c) G. Jones, II, and H. H. Kleinman, *ibid.*, 2103 (1974).
(26) The close correspondence of the yields of anthracene with those of α-methyleneoxetane and methyl vinyl ketone suggest that the olefin **15** is not further cracking to anthracene and allene to a significant extent.
(27) The following columns were used for VPC analysis: (a) 10% SF-96 on Chromosorb W, 20 ft × 0.25 in. aluminum column, (b) 10% SE-30 on Chromosorb W, 10 ft × 0.25 in. aluminum column, (c) 15% SF-96 on Chromosorb W, 5 ft × 0.25 in. stainless steel column.
(28) R. M. Nowak, *J. Org. Chem.*, **28**, 1182 (1963). For the first use of α-acetoxyacrylonitrile as a ketene equivalent in the Diels–Alder reaction, see P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956).
(29) The time was incorrectly reported as 8 hr in the preliminary communication.[9]
(30) In a separate but similar experiment, the NMR spectrum of the chromatographed product before crystallization was essentially identical with the NMR of the crystalline material.
(31) The procedure is that of M. A. Qasseem, N. A. J. Rogers, and A. A. Othman, *Tetrahedron*, **24**, 4535 (1968).
(32) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).
(33) The procedure is adapted from W. E. Bachmann, W. Cole, and A. L. Wilds, *J. Am. Chem. Soc.*, **62**, 824 (1940).
(34) This spectrum was taken of material of comparable purity from a separate but similar experiment.
(35) In a separate experiment, the crude diol **4** was chromatographed on Florisil. Elution with benzene followed by methylene chloride produced crystalline material having NMR ($CDCl_3$) δ 1.2–2.1 (m, 4.2 H), 2.1–3.5 (2 broad humps, 2.0 H), 3.5–4.0 (crude t, 2.0 H), 4.3 (broad s, 1.9 H), 7.0–7.5 (m, 9.7 H).
(36) Carbon-13 NMR spectra were determined on a Varian CFT-20 instrument; chemical shifts of the nonaromatic carbon atoms are reported in parts per million relative to tetramethylsilane (δ 0) as an internal reference, followed by the multiplicity observed with off-noise decoupling, and assignments. For consistency, compounds **4** and **7** are both numbered as shown below for compound **7**, and compounds **8** and **9** are both numbered as shown below for compound **8**.



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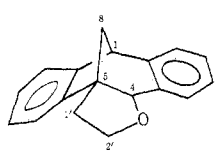

8

(37) G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, 389 (1953).
(38) Florisil (60–100 mesh) and alumina (80–200 mesh, Brockman activity 1) were obtained from Fisher Scientific Co. Silica gel (60–200 mesh) was obtained from J. T. Baker Chemical Co.
(39) The NMR spectrum was taken on a Jeol MH-100 instrument.
(40) A number of pyrolyses were also carried out by dropping crystals of **7** (100–200 mg) directly through a 2.2 × 35 cm Vycor tube packed with short lengths of 5-mm Vycor tubing, at temperatures from 400 to 800° and 0.18–1-mm pressures. Anthracene, recovered **7**, **8**, **15**, allene, and formaldehyde were among the products detected in these pyrolyses, but little or no α-methyleneoxetane was formed.
(41) NMR spectra were obtained on Varian T-60 and HA-100 spectrometers. For the NMR spectra of compounds related to **11**, see ref 5c and L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, pp 184–190, 278–279.
(42) In a similar experiment [NMR (C_2Cl_4) showed less methyl vinyl ketone] VPC analysis (SE-30, 36°)[27b] showed (in addition to solvent) the major peak at 4.4 min with a shoulder at 4.0 min and a peak at 7.1 min (cyclohexane). Cyclobutanone under these conditions had a retention time of 6.05 min. See also ref 45.
(43) An NMR spectrum was taken before chromatography to ascertain that the products isolated were not formed during the chromatography.
(44) From separate pyrolyses, careful chromatography of the nonvolatile residue produced samples of the rearranged product **8** as an oil, having essentially identical ir and NMR spectra with those of the crystalline sample of **8** prepared earlier. Pure crystalline samples of anthracene and **7** were similarly isolated.
(45) The mass spectrum of **11** was obtained on a Hitachi Perkin-Elmer Model RMU-7 instrument in conjunction with a Perkin-Elmer Model 881 gas chromatograph using a 10% SE-30 column (10 ft × 0.25 in.) at 68°, helium flow about 78 ml/min. VPC analysis showed peaks at 4.7 (corresponding in retention time to the ether solvent) and 9.1 min. The mass spectrum was taken of the material represented by the 9.1-min peak. THF under these conditions had a retention time of 9.7 min.
(46) The procedure is essentially that of G. Wittig and U. Schoellkopf, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 751.
(47) N. L. Drake and P. Allen, Jr., "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 77.
(48) Biphenyl was shown to be present in the phenyllithium solution.
(49) The product mixture from a similar reaction of phenyllithium with the distillate from the pyrolysis of **7** in benzene solvent was used. The composition of this mixture was similar by VPC to that of the reaction in THF.

Carbon-13 Spectra of Methoxyflavones

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Assignments of NMR chemical shifts for carbon of flavone, chromone, and seven methoxyflavones are reported. Qualitatively, the upfield shift induced by the methoxyl substituent is similar to that indicated by the shielding relationships given in major texts. However, the effect of methoxyl appears to be larger in compounds where important resonance forms can be written indicative of a high degree of double-bond character. The use of ^{13}C–H splittings of the various carbons to elucidate the position of substitution is covered. Splittings due to a proton meta to a given carbon are quite large (~8 Hz) and are very useful, but splittings due to ortho and para protons are irregular and of little use.

One great advantage of ^{13}C NMR spectroscopy has been in the characterization of aromatic and pseudoaromatic compounds, whose proton spectra are not well differentiated. This work is concerned with the application of ^{13}C spectroscopy to structure elucidation in a common class of naturally occurring compounds, namely, the flavones.

Proton NMR spectra of flavanoids have been studied in many laboratories since the first extensive correlation of aromatic proton signals in 1962.[1] Other studies described the use of deuterated dimethyl sulfoxide as a solvent for polyhydroxyflavones,[2] and trimethylsilylation as solubilization techniques for NMR analysis of flavanoids.[3] Several aspects of flavone NMR spectra have continued to be of interest, including an extensive study of the effect of acidic media.[4a] Solvent-induced shifts are a valuable technique for study of polysubstituted flavones.[4b] Detailed reviews of flavone NMR spectra are available.[5] Apparently no systematic ^{13}C NMR studies of the flavanoids have appeared, however.[6] The ^{13}C correlations reported herein complement these other techniques and should provide future in-

Table I
^{13}C Chemical Shifts of Isomeric Methoxyflavones[c]

Registry no.	Compd	Subst	CH_3O	2'	3'	4'	5'	6'	3	5	6	7	8	4a	8a	CO	Other
525-82-6	1	Flavone		126.0	128.8	131.3	128.8	126.0	107.3	125.4[a]	124.9[a]	133.5	117.9	123.7	156.0	178.0	131.5 163.0
491-38-3	1a	Chromone[e]							112.7	125.5[a]	124.9[a]	133.4	117.9	124.6	156.2	177.1	*f*
19725-47-4	2	2'-CH_3O	55.6	157.8	111.6	132.2	120.5	129.1	112.5	125.4[a]	124.6[a]	133.3	117.8		156.2	178.7	120.7 160.6
53906-83-5	3	3'-CH_3O	55.3	111.5	159.7	116.9[b]	129.8	118.5[b]	107.5	125.4[a]	124.9[a]	133.2	117.9[b]	123.7	155.9	178.0	132.8 162.8
4143-74-2	4	4'-CH_3O	55.3	127.7	114.2	162.1	114.2	127.7	105.9	125.3[a]	124.7[a]	133.0	117.7	123.7	155.8	177.9	*d* 163.0
42079-78-7	5	5-CH_3O	56.3	125.6	128.6	131.0	128.6	125.6	108.7	159.4	109.8	133.4	106.2	~114	157.9	177.8	131.9 160.6
26964-24-9	6	6-CH_3O		126.1	128.9	131.3	128.9	126.1	106.7	104.8		123.6	119.4				
22395-22-8	7	7-CH_3O	55.9	125.8	128.7	131.1	128.7	125.8	107.2	126.7	114.1	163.7	100.2	117.6	157.7	177.4	131.6 162.6
26964-26-1	8	8-CH_3O	56.2	126.1	128.7	131.2	128.7	126.1	107.1	114.2	124.6	116.1	148.8	~124	~146	178.0	131.6 162.6

[a] Tentative assignment only. These pairs may be interchanged. [b] Tentative assignment only. [c] In deuteriochloroform solution, at 25.2 MHz vs. tetramethylsilane [taken as 76.9 ppm from deuteriochloroform (center)]. [d] Nothing at ~132 ppm. [e] Chromone lacks ring B. [f] C_2 occurs at 155.0 ppm.

vestigators with a battery of powerful techniques that can be applied to structure elucidation.

The ^{13}C chemical shift assignments relative to TMS for flavone, chromone, and seven methoxy derivatives are given in Table I. Some of these data are reproduced with the compound in question in Scheme I. The 3-methoxy isomer was not available for this study; however, substitution in the 3 position is easily determined by proton NMR since the conspicuous peak for H-3 is missing.[5] In these ^{13}C spectra, certain carbons have very similar chemical shifts, e.g., C-5 and C-6 in compounds **1–4.** Specific assignments cannot be made for these carbons. Compound **3** also has several carbons that absorb on or near 118 ppm. Specific assignments await deuteration studies.

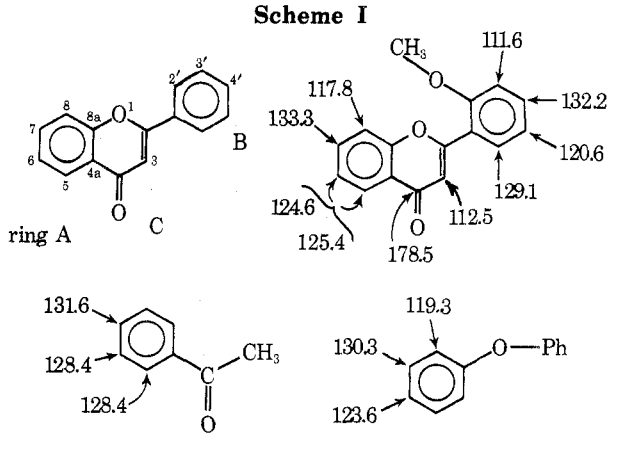
In most other cases, specific assignments were possible using the known effect of a methoxyl group upon the resonances of ortho and para carbon atoms, as shown by Lauterbur[7] and also Spiesecke and Schneider,[8] and now tabulated in major texts.[9,10] In simple benzene derivatives, carbons ortho to methoxyl are shielded by ~15 ppm and para carbons are shielded by ~9 ppm. Meta carbons are only slightly affected. Thus, a sequential change of the position of methoxyl group around rings B and A will result in a sequential shielding of carbons which are in an ortho position to methoxyl (Table I).

Of equal use in assigning resonances to specific carbons were splittings observed in high-resolution coupled spectra. The off-resonance technique was of little use. As shown by Weigert and Roberts,[11] protons meta to a given ^{13}C split the signal for that carbon by ~7 Hz. For example, the coupled spectrum of **5** (5-methoxyflavone) shows a double triplet for the resonance assigned to C-4′ (Figure 1). The widely spaced doublet (^1J = 161 Hz) is due to the proton directly attached to C-4′. The triplet into which each of the arms of the doublet is split (^3J ~ 7 Hz) indicates that C-4′ is meta to two hydrogens. In another example, for compound **5,** the resonance for C-7 appears as a 'simple' doublet (^1J = 164 Hz), indicating no meta hydrogens; this resonance can be assigned only to C-7 or C-3 (since this resonance disappears altogether in **7,** it must be due to C-7). In compounds **5–8,** C-2′ (C-6′) and C-3′ (C-5′) appear as multiplets due to the non-first-order nature of the couplings (essentially X of a AA′XX′ system is observed).

The splitting patterns for carbons 5–8 are also informative. These carbons are split either into doublets (^1J ~ 165 Hz) or double doublets depending on whether or not the position meta to the carbon in question is substituted by methoxyl.

As Scheme I shows, C-7 is strongly affected by the influence of the carbonyl (C-7 is 5 ppm more deshielded than benzene, and 2 ppm more deshielded than the para carbon

Scheme I



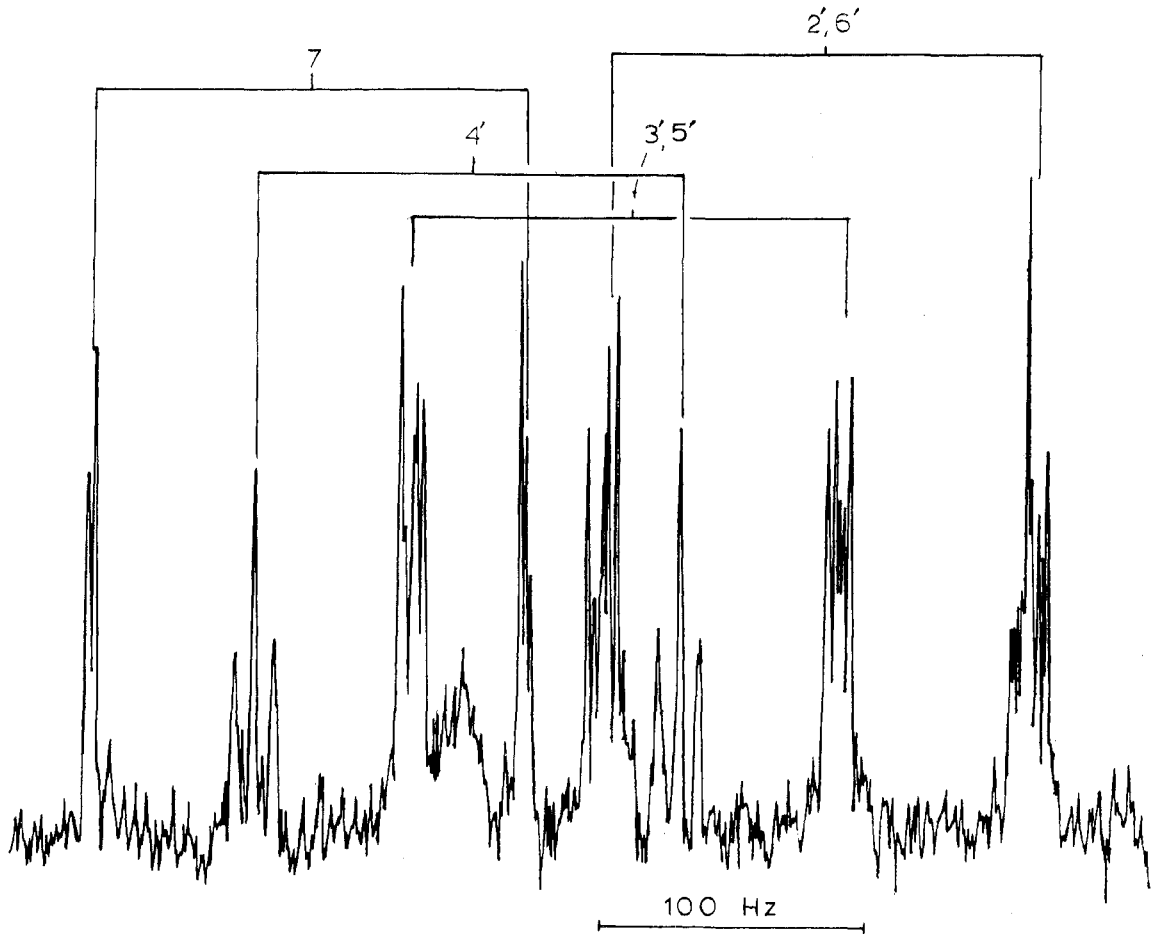


Figure 1. Portion of the coupled ^{13}C spectrum of **5**, showing the doublet of triplets pattern for C(4′).

of acetophenone). However, C-5 is 3 ppm more shielded than benzene or the ortho carbon of acetophenone, perhaps owing to a steric effect between H-5 and CO. Resonance with carbonyl renders C-5 and C-7 electron deficient, which should cause deshielding of these carbons. On the other hand, C-6 and C-8 are much more shielded than benzene owing to resonance with O-1, which increases electron density at these carbons. The chemical shifts of C-6 and C-8 are less extreme than those of para and ortho carbons of anisole, but the shifts are rather similar to those found in diphenyl ether (Scheme I). Similar to diphenyl ether, the nonbonded electrons at oxygen are delocalized into more than one ring; in flavone these electrons are required to support a degree of aromaticity in ring C, and the nonbonded electrons are relatively unavailable for delocalization into ring A.

The weak peaks due to carbons not directly bonded to hydrogen were somewhat difficult to observe under high-resolution coupled conditions, and in other cases they were buried under larger absorptions. However, if these peaks can be located, and observed with sufficient resolution, they can afford a great deal of structural information, especially concerning substitution in ring A. In ring A, the data from the intense peaks for C-5–C-8 often do not permit a decision between two possible structures. For example, under coupled conditions, C-8a appeared to be a triplet (each member of the triplet also had considerable fine splitting) except for compounds **5** and **7**. In **7**, the splitting was indistinct, but it clearly was not a triplet. In **5**, the pattern for C-8a was a clear double doublet ($^3J \sim 6$, $^2J \sim 1$ Hz), since one position meta to C-8a was blocked by the substituent. Carbon 8a occurs in a region of the spectrum (~156 ppm) in which it will not be buried by larger peaks, but it occurs close by the resonance of C-2 (~162 ppm), which has a similar appearance in some cases. The triplet for C-2 in **2** (Figure 2), however, has a narrower spacing (~3 Hz). Evidently C-2 is coupled to protons in ring B.

Carbon 4a can also yield information about the substitution pattern in ring A, but it is frequently obscured by larger peaks. For example, in compounds **5** and **7**, C-4a is shifted upfield from its usual position at 123 ppm by 10 and 6 ppm, respectively. This shift is again the effect of the methoxyl substituent. In **4**, C-4a was a clear double triplet. The ^3J values of ~7 Hz observed in the triplet showed C-4a to be meta to two hydrogens. On the other hand, in **8**, C-4a appeared as a double doublet ($^3J \sim 7$, $^2J \sim 1$), since one meta position is filled.

Generally speaking, the small splittings of a given carbon by ortho or para hydrogens (^2J and ^4J, both ~1 Hz) were in evidence in some cases and not in others. These small splittings were of no use owing to their irregular incidence.

The methoxyl absorption (56 ppm) was relatively invariant, and offers no structural information. In a more highly substituted flavone, however, steric shifts should be in evidence for these carbons. The carbon substituted by methoxyl is highly deshielded, like C-8a. Under coupled conditions, the peak due to the methoxylated carbon was broad and ill defined (Figure 2). This also occurred in certain model compounds such as anisic acid. The broadness is believed to be due to a three-bond coupling to the methoxyl hydrogens in addition to couplings to several ring hydrogens. Thus, this carbon is easily identified among other low-intensity (but sharper) absorptions.

The chemical shift for carbonyl (~178 ppm) is quite constant in **1**–**8** (cf., however, **9** and **10**). This chemical shift occurs far upfield from the carbonyl resonances in model ke-

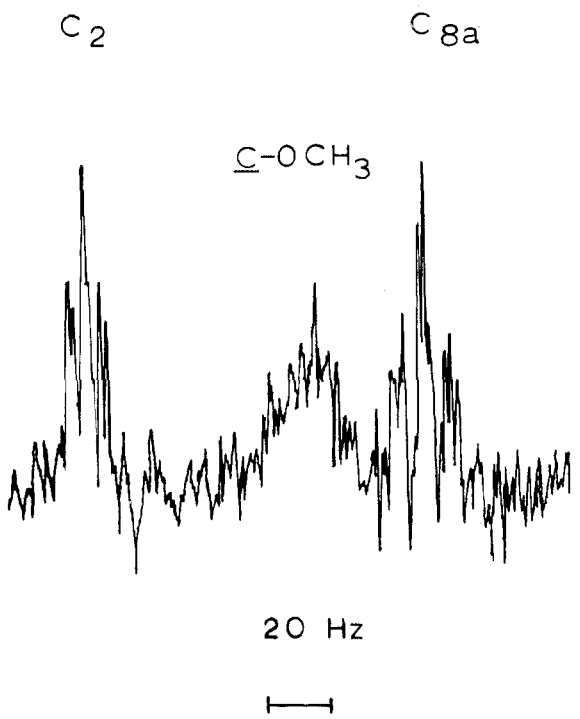


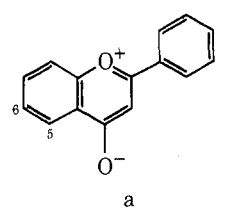
Figure 2. Portion of the coupled ^{13}C spectrum for **2**, showing the similarity of the splitting patterns for C(2) and C(8a).

tones such as acetophenone (196 ppm). This shift (18 ppm) is slightly larger than that in other α,β-unsaturated ketones (~12 ppm), which may reflect the fact that this carbonyl is part of a vinylogous ester function.[12]

The upfield shifts induced by ortho methoxyl groups are rather irregular in moving from compound to compound. A C-2′ methoxyl group shifts C-3′ ~17 ppm upfield, and C-1′ ~12 ppm upfield. A C-3′ methoxyl group shifts C-4′ 14 ppm and C-2′ 14 ppm. A C-4′ methoxyl group shifts C-3′ 15 ppm. Thus, for ring B, the upfield shifts are similar to those found for simple benzene derivatives ± 3 ppm.

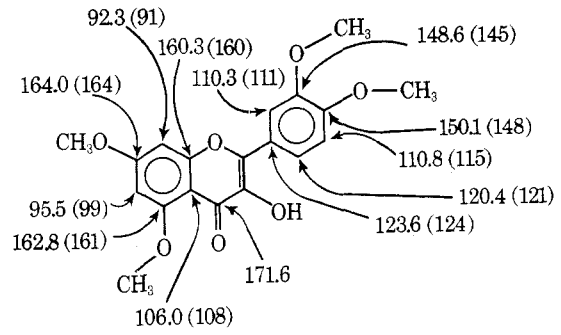
However, the methoxyl substitution in ring A results in a rather larger spread of shifts. Thus a C-5 methoxyl shifts C-6 15 ppm, but C-4a is shifted only 10 ppm. A C-6 methoxyl shifts C-7 only 10 ppm, but C-5 is shifted 20 ppm. A C-7 methoxyl shifts C-8 18 ppm, but C-6 is shifted only 11 ppm. Finally, a C-8 methoxyl shifts C-8a only 10 ppm, but C-7 is shifted 17 ppm. Thus, the shifts determined for simple benzene derivatives (15 ppm for methoxyl) should be applied for substituents in ring A with caution.

Structure a represents a presumably quite stable resonance form of flavone, as both ring A and ring C have a stable benzenoid arrangement of double and single bonds. It is noteworthy that methoxyl substitution in ring A at a given carbon will cause a large shift of the ortho carbon if the two carbons are joined by bonds of predominantly double-bond character, e.g., C-5 and C-6. On the other hand, if two carbons are joined by a bond of predominantly single-bond character, methoxyl substitution seems to result in a small shift (e.g., C-6 and C-7). However, the tentative idea that bond localization affects the degree of shielding awaits verification in other systems. However, similar effects occur in certain substituted thiophenes.[13]



a

Scheme II



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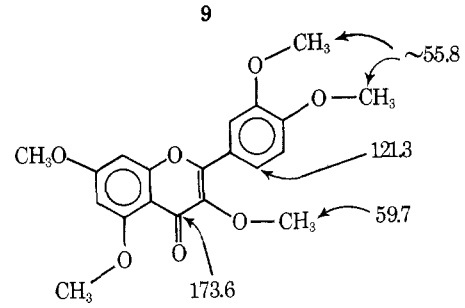

10

The usefulness of the data listed in Table I depends upon whether it can be applied to other, more highly substituted flavones. As a test, the spectra of a polymethoxylflavone, **9**, and its close relative, **10**, were run. For a carbon at position x, a methoxyl at position y will have a certain effect and a substituent at position z will have a different effect. The sum of these effects, as derived from the data in Table I, is given in Scheme II beside the observed chemical shift. Thus, for C-5, the basic chemical shift (from compound **5**) is 159.4. The effect of a C-7 methoxyl group on C-5 is +1.4 ppm. The net chemical shift expected is ~161 ppm, very close to the observed value. The agreement for most carbons is quite acceptable, but C-3′, C-5′, and C-6 show substantial deviations between the calculated and observed chemical shifts. It seems likely that steric effects in other highly substituted natural flavanoids would also cause deviations.

The C-3 hydroxyl group of **9** has become methylated in **10**. Minor changes in chemical shift were noted except for carbonyl. The C-3 methoxyl group, however, does have an anomalous chemical shift (59.7 vs. ~55.8 ppm for the other methoxyl groups).

Experimental Section

The methoxyflavones were available from other studies: **1**, mp 96–97°; **2**, mp 102–103°; **3**, mp 130–131°; **4**, mp 156–157°; **5**, mp 133–135°; **7**, mp 110–111°; and **8**, mp 200–201°. The NMR spectra were run on a Varian XL-100 instrument at 25.2 MHz. In a typical run (for **5**), a 5000-Hz spectral width was used, collecting 4K of transients, using a decoupler setting of 7 W (high power) and a 1.5K bandwidth. An acquisition time of 0.4 sec, a pulse delay of 0.1 sec, and a 30-μsec pulse were used.

The high-resolution undecoupled spectra were run either by not using the decoupler at all or using the "gated" mode of decoupler operation.[14] For **5**, the decoupler was not used. A 2500-Hz spectral width was used, with a 1.3-sec acquisition time and a 1.0-sec pulse delay, and a 30-μsec pulse width. A total of 13.5K of transients were collected. For **4**, the "gated" mode of operation was used, and a 2.5K spectral width, 0.8-sec acquisition time, and a 2.0-sec pulse delay. A total of 4.5K of transients were collected. For **6**, owing to its low concentration, the "long term averaging" routine possible with the Varian equipment was used. A spectral width of 5K was used (gated mode), using 0.8-sec acquisition time and a 2.0-sec

pulse delay. Thirty blocks of 500 transients were collected. The methoxyl quartet appeared in this run, although it was missing in the normal run even though 4096 data points were utilized.

The spectra were all run in deuteriochloroform solution at the following concentrations (percent w/v): **1**, 9.5; **2**, ca. 6; **3**, 5.5; **4**, ca. 8; **5**, 7.3; **6**, 1.8; **7**, 10.8; and **8**, 9.2. In no case did either the ^1H or the ^{13}C spectra indicate impurities. The chemical shifts were taken from the computer-generated print-out; the actual standard used was the center line of $CDCl_3$ but the data are reported vs. TMS, which was taken as 76.9 ppm from $CDCl_3$

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References and Notes

(1) J. Massicot and J.-P. Marthe, *Bull. Soc. Chim. Fr.*, 1962 (1962).
(2) T. J. Batterham and R. J. Highet, *Aust. J. Chem.*, **17**, 428 (1964).
(3) T. J. Mabry, J. Kagan, and H. Rosler, University of Texas Publication No. 6418 (1964); A. C. Waiss, R. E. Lundin, and D. J. Stern, *Tetrahedron Lett.*, 513 (1964).
(4) (a) D. Anker, C. Mercier, M. Baran-Marszak, and J. Massicot, *Tetrahedron*, **25**, 5207 (1979); (b) R. G. Wilson, J. H. Bowie, and D. H. Williams, ibid., **24**, 1407 (1968), and related papers.
(5) (a) A. Grouiller, *Bull. Soc. Chim. Fr.*, 2405 (1966); (b) T. J. Mabry, K. R. Markham, and M. B. Thomas, "The Systematic Identification of Flavanoids", Springer-Verlag New York, New York, N.Y., pp 253–343.
(6) P. Joseph-Nathan, M. C. Hernandez, J. Mares, and J. Shoolery, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, ORGN 150.
(7) P. C. Lauterbur, *J. Chem. Phys.*, **43**, 360 (1965).
(8) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **75**, 731 (1961).
(9) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 197.
(10) G. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972.
(11) (a) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2967 (1967). (b) G. Govil, *J. Chem. Soc. A*, 1420 (1967). (c) A. R. Tarpley, Jr., and J. H. Goldstein, *J. Mol. Spectrosc.*, **37**, 432 (1971); **39**, 275 (1971). (d) A note of caution should be taken from the work of Y. Takeuchi and N. Dennis, *J. Am. Chem. Soc.*, **96**, 3659 (1974), where large ^2J values were found in certain cyanopyridines (comparable to most ^3J values) for couplings involving hydrogens near nitrogen.
(12) (a) G. P. Moss, P. S. Pregosin, and E. W. Randall, *J. Chem. Soc., Perkin Trans. 1*, 1525 (1974). (b) See also K. Chexal, C. Fouweather, J. Holker, T. J. Simpson, and K. Young, ibid., 1584 (1974), who show that the chemical shift of a hydrogen-bonded carbonyl of a naturally occurring xanthone is 183 ppm. (c) N. Gurudata and J. R. Stothers, *Can. J. Chem.*, **47**, 3601 (1967). (d) R. Hollenstein and W. von Philipshorn, *Helv. Chim. Acta*, **55**, 2030 (1974).
(13) K. Takahashi, T. Sone, and K. Fujieda, *J. Phys. Chem.*, **74**, 2765 (1970).
(14) O. Gansow and W. Shittenheim, *J. Am. Chem. Soc.*, **93**, 4294 (1971).

Oxidative Decarbonylation of 2,4,6-Tri-*tert*-butylresorcinol via a Probable *m*-Quinone Intermediate

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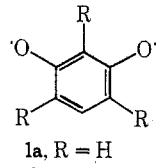
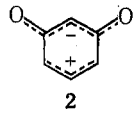
Oxidation of mixtures of 2,4,6-tri-*tert*-butylresorcinol (**4**) and its diketo tautomer (**5**) with alkaline ferricyanide at room temperature gives 2,3,5-tri-*tert*-butylcyclopentadienone (**8**) and carbon monoxide as major products. Control experiments show that these products are derived almost exclusively from **4** rather than **5**. The oxidation is suggested to involve conversion of **4** into a singlet *m*-quinone (**1b**), which cyclizes into a cyclopropanone derivative (**3b**) capable of undergoing rapid decarbonylation. This mechanism is shown to be consistent with theoretical expectations and experimental data for related systems.

In connection with other studies in this laboratory on the chemistry of phenolic antioxidants, we became interested several years ago in the properties of *m*-quinone (**1a**), the hypothetical species which would result from homolytic abstraction of the hydroxyl hydrogens of resorcinol. Our interest in **1a** was intensified, to some extent, by the results of a simple Hückel molecular orbital (HMO) calculation,[2] which predicted that **1a** would contain five nondegenerate bonding orbitals with delocalization energies of 2.314, 1.802, 1.287, 0.590, and 0.445β. Since *m*-quinone has eight π electrons, its ground-state electronic configuration was thus required to be a singlet;[3] consideration of this result, together with the bond orders and electron densities calculated for *m*-quinone by our procedure, suggested that the substance could be represented, at least to a first approximation, by the dipolar structure **2**. This species might be expected to collapse to the fully covalent structure **3a**,



1a, R = H
b, R = *t*-Bu



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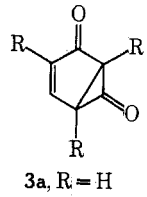
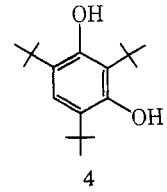


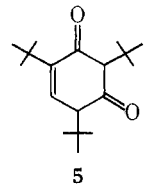
3a, R = H
b, R = *t*-Bu

which should reveal its presence by undergoing characteristic cyclopropanone reactions[4] such as nucleophilic addition or decarbonylation.

However, in view of the approximations involved in the simple HMO method, it was realized that these conclusions could not be accepted without reservation; and, in particular, it seemed that the prediction of a singlet ground state for **1a** was likely to be in error. Since the two highest bonding orbitals had been found to differ in energy by only 0.145β, it was clear that they might actually prefer to exist as a degenerate pair, owing to electron repulsions that had been neglected in the simple HMO treatment.[5] Nevertheless, thermal population of a low-lying singlet state of **1a** remained as a reasonable possibility, and we therefore decided to attempt the preparation of a suitable derivative of *m*-quinone in order to examine its chemical properties.[6] Oxidative dehydrogenation of 2,4,6-tri-*tert*-butylresorcinol (**4**) seemed especially attractive in this regard, since the *tert*-butyl groups would be expected to perturb the π system of **1b** to only a minor extent, while preventing undesirable reactions of an anticipated monophenoxy radical intermediate.[7] However, attempts to prepare **4** by direct alkylation gave 4,6-di-*tert*-butylresorcinol instead,[8] and after a brief exploration of other potential routes to **4**, its synthesis was temporarily abandoned.



4



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