6- or 8-methoxy group. Thus in the spectra of the permethylated derivatives IX and X of kaempferol and quercetin the $M-15$ peaks are 29 and 66 % of the base peaks, $(M-1)^+$ and M^+, respectively.

We now propose, that the presence of ions with the structures formally depicted as the quinoid species c and d or e and f (together with the intensive $M-15$ ions) is characteristic of 8- and 6-methoxylated flavonols, respectively. These ions, being A-ring fragments, and probably derived from a or b, are consistently found in the mass spectra of the 8- and 6-methoxylated flavonols, which have been examined (I to VIII). Their composition has been established by exact mass measurements.

Flavonols without 6- and 8-alkoxy groups do not give rise to ions with a composition corresponding to c, d, e, or f. Instead, Audier,[5] in an investigation of some flavonols, lacking alkoxy groups in the 8- and 6-positions, found another characteristic A-ring fragment, for which he proposed the structure g. This ion contains hydrogen originating from the 3-hydroxy group. In agreement with the formulation of c and d these ions did not change their masses by deuteration of the 3-hydroxy group in III (*cf.* Table 1).

It is noteworthy, that the base peak in the mass spectrum of 8-methoxy-quercetin (II) is due to the $M-15$ ion, whereas in the spectrum of 6-methoxy-quercetin (VII) it is due to the molecular ion. The opposite holds true for the permethylated derivatives of II and VII, which show M^+ and (M^+-15), respectively, as the most abundant ions.

Experimental. The mass spectra were determined by direct insertion technique with an A.E.I. MS902 mass spectrometer, operating at 70 eV and a source temperature of 200 to 250°.

1. Nielsen, J. G. *To be published.*
2. Nielsen, J. G. *Tetrahedron Letters* **1970** 803.
3. Pelter, A., Stainton, P. and Barber, M. *J. Heterocycl. Chem.* **2** (1965) 262.
4. Bowie, J. H. and Cameron, D. W. *Australian J. Chem.* **19** (1966) 1627.
5. Audier, H. *Bull. Soc. Chim. France* **1966** 2892.

Received August 5, 1970.

A Useful Method for Structure Determination of 3,3'-Bithienyls by PMR. II*

ROLF HÅKANSSON and ERIK WIKLUND

Chemical Center, Division of Organic Chemistry, University of Lund, Box 740, S-220 07 Lund 7, Sweden

In 2- and 3-carbomethoxythiophenes and in 5,5'-dicarbomethoxy-3,3'-bithienyls, the OCH_3-resonance occurs within the small interval of $6.10-6.20$ τ (CS_2) but is shifted $0.2-0.3$ ppm upfield when the carboxylic ester groups are situated at the 2,2'- or 4,4'-positions.[1] Various reasons for this were discussed, and although the observed shifts exhibited by the OCH_3 protons of carbomethoxy groups in the positions *ortho* to the pivot bond could be explained in terms of anisotropy effects from the aromatic rings, it could not be excluded that two carboxylic ester groups in a symmetrically substituted 3,3'-bithienyl might shield each other, or that another *ortho* substituent might affect the conformation of the carbomethoxy group relative to the bithienyl skeleton, and thus cause a shift of the OCH_3 protons.

In connection with other work on 3,3'-bithienyls some 3,3'-bithienylmonocarboxylic acid were prepared together with their methyl esters.[2,3] The latter were investigated by PMR and the shifts of the OCH_3 protons are collected in Table 1 together with the τ_{OCH_3}-values of some dicarbomethoxy compounds of interest for comparison.

The data in Table 1 show that even in unsymmetrically substitued 3,3'-bithienyls with only one carbomethoxy group in the molecule at the 2- or 4-position, the OCH_3-resonance is shifted upfield to about the same extent as in symmetrically substituted 2,2'- or 4,4'-dicarbomethoxy-3,3'-bithienyls. This decreases the plausibility of the suggestion that the shift might arise from the mutual shielding of two carbomethoxy groups, and makes it unlikely that the main part of the upfield shift is caused by shielding of other *ortho* substituents since in that case the shift would be more sensitive to the nature of such substituents.

* For Part I see Ref. 1.

Table 1. Chemical shifts of the OCH_3 protons of some carbomethoxy-3,3'-bithienyls in CS_2 (2 % TMS).

No.	Ester	τ	Ref.
1	2-Carbomethoxy-3,3'-bithienyl	6.30	
2	—, 2'-bromo	6.33	3
3	—, 2',4,4'-tribromo	6.32	3
4	—, 2'-bromo-5,5'-dimethyl	6.39	3
5	—, 2'-bromo-4,4',5,5'-tetramethyl	6.43	3
6	—, 2'-hydroxymethyl-4,4'-dimethyl	6.44	4
7	—, 4,4'-dibromo-2'-hydroxymethyl	6.33	2
8	4-Carbomethoxy-3,3'-bithienyl	—	
9	—, 4'-bromo-5,5'-dimethyl	6.52	3
10	—, 4'-bromo-2,2',5,5'-tetramethyl	6.53	3
11	—, 4'-hydroxymethyl-2,2'-dimethyl	6.52	4
12	—, 2,2'dibromo-4'-hydroxymethyl	6.39	2
13	5-Carbomethoxy-3,3'-bithienyl	—	
14	—, 4,4',5'-tribromo	6.17	3
15	2,2'-Dicarbomethoxy-3,3'-bithienyl	6.40	3
16	—, 4,4'-dibromo	6.36	1
17	—, 4,4'-dimethyl	6.40	5
18	—, 5,5'-dimethyl	6.44	3
19	—, 4,4'5,5'-tetramethyl	6.48	3
20	4,4'-Dicarbomethoxy-3,3'-bithienyl	6.49	6
21	—, 2,2'-dibromo	6.44	2
22	—, 2,2'-dimethyl	6.45	4
23	—, 5,5'-dimethyl	6.56	3
24	—, 2,2',5,5'-tetramethyl	6.58	3
25	4-Bromo-2,4'-dicarbomethoxy-5,5'-dimethyl-3,3'-bithienyl	6.48	3
		6.54	
26	5,5'-Dicarbomethoxy-3,3'-bithienyl	—	
27	—, 4,4'-dibromo	6.17	3
28	—, 2,2',4,4'-tetramethyl	6.24	7

Thus comparison between compounds *3* and *16* shows that exchanging the 2'-carbomethoxy group in *16* for bromine causes a downfield shift of only 0.04 ppm. The same is found for *5* and *19* (0.05 ppm), *9* and *23* (0.04 ppm), and for *10* and *24* (0.05 ppm). The largest difference, 0.07 ppm, is found for compounds *2* and *15*. If in the dibromo compounds *7* and *12* the hydroxymethyl groups are replaced by carbomethoxy groups, the OCH_3-resonance is shifted upfield 0.03 — 0.05 ppm (see *16* and *21*), but in the dimethyl compounds *6* and *11* the same operation causes a downfield shift of 0.04 — 0.07 ppm (see *17* and *22*).

In order to more closely elucidate the importance of *ortho* substituents, 2-carbomethoxy-3,3'-bithienyl (*1*) was prepared.

Its methoxyl resonance was found at 6.30 τ, and this value is 0.12 ppm higher than that for 2-carbomethoxythiophene.[1] A bromine atom at the 2'-position of *1* causes a shift of 0.03 ppm (*2*, Table 1), and a second carbomethoxy group in this position gives a τ_{OCH_3}-value which is 0.10 ppm higher (*15*).

The upfield shifts for carbomethoxy groups at the 2- or 4-position in 3,3'-bithienyls are best explained in terms of anistropy effects from the aromatic ring at the 3-position. The smaller differences in chemical shifts pointed out above may arise from variations of the interplanar angle of twist in the bithienyl skeleton, or alterations of the conformation of the carboxylic ester groups, in both cases caused by interactions between the substituents in the two aromatic rings. The consequences of this were discussed previously.[1]

The small difference between the unusually high value of 6.24 τ found for the 5,5'-dicarbomethoxy compound *28* and 6.30 τ for the 2-carbomethoxy compound *1* would appear to make the assignment of structures to carbomethoxy-3,3'-bithienyls by PMR spectroscopy somewhat uncertain. However, compound *28* should be compared to other tetramethyl-3,3'-bithienyls such as *19* and *24*. The value for *19*, 6.48 τ, is one of the highest found for carbomethoxy groups at the 2-position in 3,3'-bithienyls and that for the 4,4'-dicarbomethoxy compound *24*, 6.58 τ, is the highest ever observed in this connection. This is in accordance with the electron-donating properties of methyl groups.[8]

The difference between the chemical shifts of a carbomethoxy group at the 5-position and at the 2- or 4-position of 3,3'-bithienyl thus makes PMR spectroscopy a useful method for assigning structures to this system in general, and the discussion in this connection in the previous paper[1] may now be extended to unsymmetrically substituted 3,3'-bithienyls. For example, it was recently found that reacting 4,4'-dibromo-3,3'-bithienyl with one equivalent of alkyllithium followed by carbonation yielded 4,4'-dibromo-5-carboxy-3,3'-bithienyl.[3] The structure of the product was easily determined since the OCH_3-resonance of the corresponding methyl ester obtained with diazomethane occurred at 6.17 τ, clearly showing the carboxylic ester group to be situated at a 5-position (*cf.* also *14* and *27*).

In this case it would have been laborious to determine the position of the carbomethoxy group by other methods.

It was found that some compounds, and especially *15*, were rather insoluble in carbon disulphide. The aromatic hydrogen resonances were not detectable in the PMR spectrum, but the methoxyl resonance could still be determined with certainty. This may limit the use of PMR in analyses of product mixtures.

Experimental. 2-Carboxy-3,3'-bithienyl. To 2.0 g (0.012 mole) of 3,3'-bithienyl in 80 ml of acetic acid-chloroform (1:1) at room temperature was added 2.0 g (0.011 mole) of *N*-bromosuccinimide. After 5 min the mixture was diluted with water, the organic layer was separated and washed with water, aqueous sodium carbonate solution and again with water, dried and the solvent evaporated. 2.7 g of crude *2-bromo-3,3'-bithienyl** was obtained as an oil which crystallized on cooling in a dry ice-acetone bath but melted again on warming to room temperature. The oil was dissolved in 75 ml of anhydrous ether in a nitrogen-swept apparatus, the solution was cooled to −70° and 13 ml of 1.0 M butyllithium was added. After 3 min the mixture was carbonated with gaseous carbon dioxide, hydrolyzed with water and the layers separated. Acidification of the water phase yielded 1.9 g (75 %) of crude 2-carboxy-3,3'-bithienyl. The IR-spectrum showed the absence of 2-bromo-2'-carboxy-3,3'-bithienyl,[3] which has a sharp peak at 995 cm^{-1}, but the presence of smaller amounts of 2,2'-dicarboxy-3,3'-bithienyl[3] (at 1095 cm^{-1}, 1160 cm^{-1}, and 1570 cm^{-1}). Recrystallizations from ethanol-water (yield: 1.4 g) and acetic acid (yield: 0.6 g) did not change the IR spectrum. Evaporation of the last mother liquor yielded 0.75 g whose IR spectrum exhibited a split carbonyl band and the absence of dicarboxylic acid. The analytical sample, m.p. 166−167°, was further recrystallized from acetic acid. (Found: C 51.2; H 2.97;

---

* The structure assigned follows from the mode of preparation. Addition of the double amount of *N*-bromosuccinimide yields 2,2'-dibromo-3,3'-bithienyl.[9]

S 30.5. Calc. for $C_9H_6O_2S_2$ (210.3): C 51.41; H 2.88; S 30.50).

2-Carbomethoxy-3,3'-bithienyl was obtained from 2-carboxy-3,3'-bithienyl with diazomethane; m.p. 74−75° (from ligroin, b.p. 65−75°). PMR: $\tau_{OCH_3} = 6.30$ ppm, $\tau_{arom.} = 2.3−3.0$ ppm (complex pattern). (Found: C 53.5; H 3.66; S 28.5. Calc. for $C_{10}H_8O_2S_2$ (224.3): C 53.55; H 3.59; S 28.59).

The PMR spectra were recorded on a Varian A-60 spectrometer using CS_2 solutions saturated with the test compound or containing 15 % of sample. The magnet sweep was calibrated using a Hewlett Packard wide range oscillator model 200 CD. The frequency was measured with a Hewlett Packard electronic counter model 3734 A. The IR spectra were recorded on a Perkin-Elmer 257 grating infra-red spectrophotometer. Melting points were taken on a hot stage microscope.

1. Håkansson, R. *Acta Chem. Scand.* **23** (1969) 952.
2. Wiklund, E. and Håkansson, R. *Acta Chem. Scand.* **24** (1970) 341.
3. Håkansson, R. *Acta Chem. Scand.* To be published.
4. Wiklund, E. and Håkansson, R. *To be published.*
5. Gronowitz, S. and Hagen, S. *Arkiv Kemi* **27** (1967) 153.
6. Gronowitz, S. *Acta Chem. Scand.* **15** (1961) 1393.
7. Wiklund, E. and Håkansson, R. *Paper in preparation.*
8. Gronowitz, S. In Katritzky, A. R. *Advan. Heterocyclic Chem.* **1** (1963) 1.
9. Kellogg, R. M., Schaap, A. P. and Wynberg, H. *J. Org. Chem.* **34** (1969) 343.