

## Fatty Acids, Part 28.<sup>1</sup> <sup>1</sup>H- and <sup>13</sup>C-Nuclear Magnetic Resonance Studies of 2,5-Disubstituted C<sub>18</sub> Furanoid Ester Isomers

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The <sup>1</sup>H n.m.r. spectra of all positional isomeric C<sub>18</sub> furanoid fatty esters and the <sup>13</sup>C n.m.r. spectra of 12 isomers of the same series are reported. The chemical shifts of the protons and carbons of the methylene groups located between either the methoxycarbonyl and furan system or methyl group and furan system permit facile characterization of the positional isomers. The chemical shifts of the ring protons and carbons provide further confirmation of the characterization of the isomers.

In the course of our investigations into the chemical and physical behaviour of long-chain furanoid fatty acid esters,<sup>2-4</sup> we have made a detailed <sup>1</sup>H- and <sup>13</sup>C-n.m.r. study of a series of 14 positional isomeric C<sub>18</sub> furanoid fatty esters (**1**).

Our interest in the furanoid fatty acids arises from their presence in fish lipids<sup>5,6</sup> and in the latex of the rubber plant (*Hevea brasiliensis*).<sup>7,8</sup>

In general, <sup>13</sup>C n.m.r. chemical shifts are more responsive than those from <sup>1</sup>H n.m.r. spectra to changes in the locations of functional groups in the alkyl chains of fatty acids, and are therefore more informative about the positions of such groups.<sup>9-11</sup> The present investigation will show whether this is also the case with a furan ring.

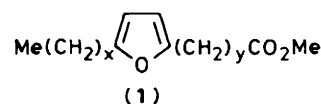
All C<sub>18</sub> furanoid esters (**1**) under investigation were synthesized as reported elsewhere.<sup>3</sup>

### Results and Discussion

All chemical shifts ( $\delta$ ) are in p.p.m. with SiMe<sub>4</sub> as an internal standard.

<sup>1</sup>H N.m.r. Spectral Assignments.—The chemical shifts of the various protons of the fourteen C<sub>18</sub> furanoid esters are given in Table 1. The <sup>1</sup>H n.m.r. spectra of numerous furan compounds, and the substituent effects on the chemical shifts and coupling constants, have been well documented,<sup>12</sup> and these spectral assignments were used where applicable. The spectra of some furanoid esters have been reported,<sup>13-16</sup> and it is known that the appearance of a two-proton signal at  $\delta$  ca. 5.70 (3-H and 4-H) confirms the presence of the 2,5-disubstituted furan system.

The characteristic signal due to the protons of the methyl ester (methoxycarbonyl) group appears as a singlet at  $\delta$  ca. 3.6 for all positional isomers except for compounds (**1a**) and (**1b**), where the signals are shifted to 3.83 and 3.70 p.p.m., respectively. In isomer (**1a**), the furan nucleus is attached directly to the CO<sub>2</sub>Me group, resulting in conjugation of the  $\pi$ -electrons of the CO<sub>2</sub>Me group with the heteroaromatic system, causing a significant downfield shift of the methyl protons signal. In compound (**1b**), the effect of the furan system on the chemical shift of the methyl protons of the ester group is diminished by the methylene group separating the ester and the furan system. The influence of the furan nucleus on the chemical shift of the  $\omega$ -methyl protons of the alkyl chain is distinguishable even with 3 methylene groups between the  $\omega$ -methyl group and the furan system, as in isomer (**1j**), where the signal appears at  $\delta = 0.94$  instead of the normal  $\delta = 0.89 \pm 0.01$  position. As the distance between the furan nucleus and the  $\omega$ -end of the alkyl chain decreases, this effect increases; e.g., the signals for the  $\omega$ -



|                  |                  |
|------------------|------------------|
| a; x = 12, y = 0 | h; x = 5, y = 7  |
| b; x = 11, y = 1 | i; x = 4, y = 8  |
| c; x = 10, y = 2 | j; x = 3, y = 9  |
| d; x = 9, y = 3  | k; x = 2, y = 10 |
| e; x = 8, y = 4  | l; x = 1, y = 11 |
| f; x = 7, y = 5  | m; x = 0, y = 12 |
| g; x = 6, y = 6  | n; †, y = 13     |

† No substituent at position 5 of the furan ring.

methyl protons appear at  $\delta = 1.21$  and  $\delta = 2.22$  for isomers (**1l**) and (**1m**), respectively. The coupling constant  $J$  between the Me and CH<sub>2</sub> protons is also clearly affected by the approaching furan ring ( $7.4 \pm 0.1$  instead of the normal  $6.7 \pm 0.1$  Hz).

Not only does the heteroaromaticity of the furan nucleus affect the neighbouring protons, but the methoxycarbonyl group also exerts a similar effect on the two protons of the furan system. The signals of the 3- and 4-position ring protons of such 2,5-disubstituted C<sub>18</sub> furan esters appear at  $\delta = ca. 5.7$  when unaffected by the ester group, as in isomers (**1g**)—(**1m**). The ring protons are shifted to 6.97 and 6.05 p.p.m. in isomer (**1a**), as the ester group is conjugated with the furan ring, while a smaller but significant effect is exerted on the ring protons of isomer (**1b**) by the ester group, producing signals at  $\delta = 5.95$  and 5.75. With  $\geq 1$  methylene group(s) between the ester group and the furan system, the downfield shift effect of the ester group on the ring protons subsides rapidly, as seen in compounds (**1c**)—(**1f**). In compounds (**1a**)—(**1f**), the differences in  $\delta$  are large enough to observe two doublets with coupling constants of 3.0—3.5 Hz.

Of greater importance are the combined effects of ester and furan, or  $\omega$ -methyl and furan groups, on the chemical shifts of the methylene protons between these groups. The 2-H protons of compound (**1b**) appear as a singlet at  $\delta = 3.48$ . Isomer (**1c**) provides distinct triplets at 2.55 and 2.87 p.p.m. for 2-H and 3-H protons. The quintuplet signal at  $\delta = 1.91$  characterizes isomer (**1d**) by its 3-H protons. Isomers (**1e**)—(**1i**) become indistinguishable as the chemical shifts of the various sets of methylene protons overlap extensively. Compound (**1j**) gives a sextet at  $\delta = 1.37$  ( $J$  7.5) for 17-H protons, while isomer (**1k**) is distinguished by a signal at  $\delta = 1.64$  (sext.,  $J$  7.3) for 17-H protons. With one methylene group between the furan ring and the  $\omega$ -methyl group, the 17-H protons of compound (**1l**) appear as a distinct quartet at  $\delta = 2.57$  ( $J$  7.5). Lastly, compound (**1n**)

Table 1. <sup>1</sup>H N.m.r. chemical shifts (δ) of C<sub>18</sub> furanoid methyl fatty esters

| (1) Positional Isomer | CO <sub>2</sub> Me | 2-H       | 3-H                         | 4-H              | 5-H                           | 6-H                           | 7-H                           | 8-H                           | 9-H | 10-H | 11-H | 12-H | 13-H                        | 14-H                 | 15-H      | 16-H             | 17-H             | 18-H             |
|-----------------------|--------------------|-----------|-----------------------------|------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----|------|------|------|-----------------------------|----------------------|-----------|------------------|------------------|------------------|
| <b>a</b>              | 3.83<br>s          |           | 6.97<br>d, J 3.5            | 6.05<br>d, J 3.5 | 2.68<br>t, J 7.5              | 1.70<br>qn, dist              |                               |                               |     |      |      |      | 1.1—1.5<br>c                |                      |           |                  |                  | 0.90<br>t, J 6.6 |
| <b>b</b>              | 3.70<br>s          | 3.48<br>s | 5.95<br>d, J 3.5            | 5.75<br>d, J 3.5 | 5.75<br>d, J 3.5              | 2.53<br>t, J 7.5              | 1.59<br>q, br                 |                               |     |      |      |      | 1.2—1.4<br>c                |                      |           |                  |                  | 0.90<br>t, J 6.6 |
| <b>c</b>              | 3.63<br>s          | 2.55<br>s | 2.87<br>t, J 7.5            | 5.73<br>d, J 3.0 | 5.79<br>d, J 3.0              | 1.59<br>qn, br                |                               |                               |     |      |      |      | 1.2—1.4<br>c                |                      |           |                  |                  | 0.89<br>t, J 6.7 |
| <b>d</b>              | 3.61<br>s          | 2.27<br>s | 1.91<br>qn, J 7.0           | 2.60<br>t, J 3.0 | 5.73 <sup>a</sup><br>d, J 3.0 | 5.78 <sup>a</sup><br>d, J 3.0 | 1.59<br>qn, br                |                               |     |      |      |      | 1.2—1.4<br>c                |                      |           |                  |                  | 0.89<br>t, J 6.7 |
| <b>e</b>              | 3.60<br>s          | 2.26<br>s | 1.5—1.7<br>c                | 1.5—1.7<br>c     | 2.56<br>t, br, J 6.5          | 5.71 <sup>a</sup><br>d, J 3.0 | 5.75 <sup>a</sup><br>d, J 3.0 |                               |     |      |      |      | 1.1—1.4<br>c                |                      |           |                  |                  | 0.90<br>t, J 6.6 |
| <b>f</b>              | 3.61<br>s          | 2.24<br>s | 1.5—1.7<br>c                | 1.1—1.5<br>c     | 1.5—1.7<br>c                  | 2.54<br>t, J 7.5              | 5.71 <sup>a</sup><br>d, J 3.0 | 5.73 <sup>a</sup><br>d, J 3.0 |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 0.89<br>t, J 6.6 |
| <b>g</b>              | 3.60<br>s          | 2.22<br>s | 1.5—1.7<br>c                | 1.2—1.5<br>c     | 1.5—1.7<br>c                  | 2.52<br>t, J 7.5              | 5.71<br>d, J 3.0              | 5.71<br>c                     |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 0.88<br>t, J 6.8 |
| <b>h</b>              | 3.60<br>s          | 2.22<br>s | 1.5—1.7<br>c                | 1.2—1.4<br>c     | 1.5—1.7<br>c                  | 2.52<br>t, J 7.5              | 5.72<br>c                     | 5.72<br>c                     |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 0.90<br>t, J 6.8 |
| <b>i</b>              | 3.61<br>s          | 2.22<br>s | 1.60 <sup>a</sup><br>qn, br | 1.2—1.5<br>c     | 1.2—1.5<br>c                  | 1.58 <sup>a</sup><br>qn, br   | 5.72<br>c                     | 5.72<br>c                     |     |      |      |      | 1.2—1.4<br>c                |                      |           |                  |                  | 0.91<br>t, J 6.8 |
| <b>j</b>              | 3.61<br>s          | 2.22<br>s | 1.5—1.7<br>c                | 1.2—1.4<br>c     | 1.2—1.4<br>c                  | 1.5—1.7<br>c                  | 5.72<br>c                     | 5.72<br>c                     |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 0.94<br>t, J 6.8 |
| <b>k</b>              | 3.61<br>s          | 2.22<br>s | 1.5—1.7<br>c                | 1.2—1.4<br>c     | 1.2—1.4<br>c                  | 1.5—1.7<br>c                  | 5.72<br>c                     | 5.72<br>c                     |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 0.96<br>t, J 7.3 |
| <b>l</b>              | 3.60<br>s          | 2.21<br>s | 1.58 <sup>a</sup><br>qn, br | 1.1—1.4<br>c     | 1.1—1.4<br>c                  | 1.59 <sup>a</sup><br>t, J 7.3 | 5.71<br>c                     | 5.71<br>c                     |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 1.21<br>t, J 7.5 |
| <b>m</b>              | 3.60<br>s          | 2.22<br>s | 1.59<br>qn, br              | 1.1—1.5<br>c     | 1.1—1.5<br>c                  | 1.59 <sup>a</sup><br>qn, br   | 5.71<br>c                     | 5.71<br>c                     |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 2.22<br>t, J 7.5 |
| <b>n</b>              | 3.60<br>s          | 2.22<br>s | 1.59 <sup>a</sup><br>qn, br | 1.1—1.4<br>c     | 1.1—1.4<br>c                  | 1.59 <sup>a</sup><br>qn, br   | 5.71<br>c                     | 5.71<br>c                     |     |      |      |      | 1.5—1.7<br>c                |                      |           |                  |                  | 7.18<br>s        |
|                       |                    |           |                             | †                |                               |                               |                               |                               |     |      |      |      | 1.62 <sup>a</sup><br>qn, br | 2.58<br>t, br, J 7.3 | 5.86<br>c | 6.15<br>d, J 3.0 | 7.18<br>d, J 1.8 |                  |

<sup>a</sup> ambiguity exists: s = singlet; d = doublet; t = triplet; q = quartet; qn = quintet; sext = sextet; c = complex; br = broad; dist = distorted; J = coupling constant in Hz.

† No substituent at position 5 of the furan ring.

**Table 2.**  $^{13}\text{C}$  Chemical shifts (p.p.m.) of furanoid esters in  $\text{CDCl}_3$ 

| Isomer of (I) | C-1    | C-2   | C-3   | C-4    | C-5                | C-6                | C-7                | C-8                | C-9                | C-10               | C-11               | C-12               | C-13               | C-14               | C-15   | C-16   | C-17   | C-18   | Me    |
|---------------|--------|-------|-------|--------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------|--------|--------|--------|-------|
| c             | 173.13 | 32.76 | 23.66 | 152.17 | 105.67             | 105.09             | 155.42             | 28.11              | 28.11              | 29.28              | 29.41              | 29.67              | 29.67              | 29.67              | 29.41  | 31.98  | 22.71  | 14.10  | 51.63 |
| d             | 173.88 | 33.34 | 23.56 | 27.42  | 153.12             | 105.74             | 104.99             | 155.23             | 28.14              | 28.14              | 29.28              | 29.38              | 29.64              | 29.64              | 29.38  | 31.94  | 22.71  | 14.10  | 51.47 |
| e             | 174.04 | 33.86 | 24.53 | 27.71  | 27.71              | 153.83             | 105.28             | 104.96             | 154.97             | 28.14              | 28.14              | 29.34              | 29.42              | 29.57              | 29.42  | 31.94  | 22.71  | 14.10  | 51.44 |
| f             | 174.21 | 34.02 | 24.73 | 28.69  | 27.88              | 27.88              | 154.22             | 105.09             | 104.89             | 154.84             | 28.11              | 28.11              | 29.28              | 29.28              | 29.28  | 31.91  | 22.68  | 14.07  | 51.44 |
| g             | 174.24 | 34.12 | 24.92 | 28.95  | 28.86              | 28.04 <sup>a</sup> | 28.04 <sup>a</sup> | 154.45             | 105.06             | 104.93             | 154.84             | 28.22 <sup>a</sup> | 28.14              | 29.25              | 29.12  | 31.85  | 22.68  | 14.07  | 51.41 |
| h             | 174.30 | 34.15 | 24.99 | 29.05  | 28.95 <sup>a</sup> | 29.05 <sup>a</sup> | 28.14              | 28.14              | 154.58             | 104.93             | 104.93             | 154.77             | 28.14              | 28.14              | 29.05  | 31.68  | 22.62  | 14.07  | 51.41 |
| i             | 174.34 | 34.12 | 24.99 | 29.15  | 29.15              | 29.15              | 29.15              | 28.08              | 28.08              | 154.64             | 104.93             | 104.93             | 154.74             | 28.08              | 27.88  | 31.46  | 22.42  | 13.97  | 51.41 |
| j             | 174.27 | 34.15 | 25.02 | 29.21  | 29.21              | 29.70 <sup>a</sup> | 29.21 <sup>a</sup> | 29.34              | 28.11 <sup>b</sup> | 28.15 <sup>b</sup> | 154.64             | 104.89             | 104.89             | 154.64             | 27.82  | 30.35  | 22.32  | 13.81  | 51.37 |
| k             | 174.34 | 34.15 | 25.02 | 29.21  | 29.21              | 29.51              | 29.67              | 29.44              | 29.38              | 29.17 <sup>a</sup> | 28.11 <sup>a</sup> | 154.74             | 104.89             | 105.02             | 154.51 | 30.16  | 21.51  | 13.75  | 51.37 |
| l             | 174.34 | 34.15 | 25.02 | 29.28  | 29.28              | 29.57              | 29.57 <sup>a</sup> | 29.47 <sup>a</sup> | 29.47              | 29.28              | 28.14              | 28.14              | 155.91             | 105.15             | 104.89 | 154.77 | 21.41  | 12.25  | 51.41 |
| m             | 174.34 | 34.15 | 25.02 | 29.25  | 29.25              | 29.57              | 29.57 <sup>a</sup> | 29.45 <sup>a</sup> | 29.57 <sup>a</sup> | 29.45              | 29.25              | 28.23              | 28.14              | 154.90             | 105.15 | 105.77 | 150.06 | 13.45  | 51.37 |
| n             | 174.34 | 34.15 | 25.02 | 29.21  | 29.21              | 29.53              | 29.64              | 29.64              | 29.64              | 29.64              | 29.41              | 29.21              | 28.04 <sup>a</sup> | 28.11 <sup>a</sup> | 156.72 | 104.57 | 110.06 | 140.70 | 51.41 |

<sup>a</sup> Ambiguity remains. <sup>b</sup> Ambiguity remains.

shows the characteristics of a monosubstituted furan by displaying doublets for its 16-H and 18-H protons and a double doublet for its 17-H proton.

**Chemical Shift Parameters.**—Following a similar approach to that established by Frost and Gunstone,<sup>9,17</sup> the effect on the chemical shifts of the protons of the methylene groups exerted by the furan nucleus may be accurately described by a set of empirical shift parameters. The unperturbed  $\delta$ -value for a CH<sub>2</sub> group in an alkyl chain is 1.255 p.p.m. and for a terminal Me group  $\delta = 0.885$ .

For (R<sup>1</sup>)C=CHCH=C(R<sup>2</sup>)O the chemical shift change (p.p.m.) in a CH<sub>2</sub> group in R<sup>2</sup> (assumed to be a linear alkyl chain) caused by a replacement of (CH<sub>2</sub>)<sub>n</sub> by the furan ring substituted with R<sup>1</sup> is:  $\alpha$ , 1.266;  $\beta$ , 0.338; and  $\gamma$ , 0.074. Similarly, the chemical shift change in a Me group caused by the furan ring is:  $\alpha$ , 1.337;  $\beta$ , 0.323;  $\gamma$ , 0.073;  $\delta$ , 0.053;  $\epsilon$ , 0.028; and  $\xi$ , 0.012. If R<sup>1</sup> = H then the effect on CH<sub>2</sub> is:  $\alpha$ , 1.324, and  $\beta$ , 0.368.

All parameters indicate shifts to lower field and are, as a consequence, positive.

By way of example, we can observe that the protons of a CH<sub>2</sub> group directly bound to the furan ring (*i.e.*  $\alpha$  to the furan ring) will have a chemical shift of 1.255 + 1.266 = 2.52 p.p.m. if unperturbed by other functional groups. When the Me group is in the  $\beta$ -position with respect to the furan ring the chemical shift will be 0.885 + 0.323 = 1.21 p.p.m.

From this study it is possible to identify, with a high degree of certainty, 8 out of the 14 positional isomers without the addition of any lanthanide shift reagent.<sup>11</sup> Ambiguities do exist in assigning some of the signals, as indicated in Table 1, but this drawback does not upset the general trend of the parameters discussed.

**<sup>13</sup>C N.m.r. Spectral Assignments.**—The <sup>13</sup>C chemical shifts of 12 positional isomeric furanoid esters are given in Table 2. For the numbering system we considered the four carbon atoms of the furan ring to be a part of the fatty acid 'chain' and the ester carbonyl carbon as C-1. Referring to the substituent parameters derived from our studies of saturated and unsaturated fatty esters,<sup>10,18</sup> the assignments of the various <sup>13</sup>C chemical shifts of most of the methylene groups, unaffected by the furan system, were readily achieved.

The chemical shifts of the four carbons of the furan system are normally *ca.* 154 p.p.m. (for carbons at the 2- and 5-position) and *ca.* 105 p.p.m. (for carbons at the 3- and 4-position), but these are affected when the ring substituent is a methyl group [*viz.* (1m)], or when the furan system is affected by the proximity of the methoxycarbonyl group [*viz.* (1c)—(1e)]. A few ambiguities remain, but these are not significant enough to thwart the characterization of the furanoid isomers.

In compound (1m) the methyl group causes C-14 and C-17 to be shifted to 154.90 and 150.06 p.p.m., respectively. With a methylene group between the furan ring and the  $\omega$ -methyl group, these analogous ring carbons C-13 and C-16 are shifted to 155.91 and 154.77 p.p.m., respectively, as shown by compound (1l). The effect of the methoxycarbonyl group on the ring carbons also results in significant changes in the chemical shifts. Compound (1c), with two methylene groups between the ester and furan systems, causes C-4 and C-7 to shift to 152.17 and 155.42 p.p.m., respectively. This effect gradually diminishes when the number of methylenes increases to 5. However, the differences in the patterns in the  $\delta = 28.0$ – $30.0$  region allow us to discriminate even between the isomers (1g), (1h), and (1i). The C-16 signals of the compounds (1h)—(1k) support the identification of these four mid-chain furan isomers. The combined effect of the furan and  $\omega$ -methyl groups gives rise to significant upfield shifts of the carbons located  $\alpha$ - and  $\beta$ - to the furan system and at the same time at  $\beta$ - and  $\gamma$ - to the methyl

group. The shifts of C-15 and C-16 of (1j) are characteristic and appear at 27.82 and 30.35 p.p.m., respectively. The same effect causes distinct signals at 30.16 and 21.51 p.p.m. for C-16 and C-17 of compound (1k). Compound (1l), which has a sole methylene group between the furan ring and the methyl group, not only has C-17 shifted to 21.41 p.p.m., but the  $\omega$ -methyl carbon is also affected by its proximity to the furan nucleus, placing the shift of C-18 at 12.25 p.p.m. On the whole the  $\omega$ -methyl carbon is shifted only slightly upfield when the furan nucleus is  $\leq 4$  methylene groups away from it. Similar effects of the furan rings on the C-1 and OMe of the ester group are anticipated, but owing to the instability of isomers (1a) and (1b) no <sup>13</sup>C n.m.r. spectra have been recorded. The monosubstituted furan isomer, (1n), gave 4 distinct signals for the ring carbons, these appearing at 156.72, 104.57, 110.06, and 140.70 p.p.m. for C-15, -16, -17, and -18, respectively.

We can conclude that it is possible to identify, through a <sup>13</sup>C n.m.r. study, all positional C<sub>18</sub> furanoid esters.

### Experimental

The preparation of the C<sub>18</sub> furanoid fatty esters has been reported elsewhere.<sup>3</sup> <sup>1</sup>H N.m.r. spectra were recorded at 300 MHz with Varian HR300 and SC300 spectrometers (sited at TNO, Delft). <sup>13</sup>C N.m.r. spectra were made on a Bruker WH90 Fourier Transform spectrometer operating at 22.62 MHz with proton noise decoupling. The Nicolet B-NC 12 computer with a 20K data memory was used for the 16K or 8K free-induction decay. The resulting accuracy of the carbon chemical shifts is  $\pm 0.05$  or  $\pm 0.1$  p.p.m., respectively. The spectra (3 000–10 000 accumulations; 15–40° pulses; 28 °C) were obtained from solutions in CDCl<sub>3</sub> (0.2–0.5 mol l<sup>-1</sup>) which also served as an internal deuterium lock. All spectra were calibrated against SiMe<sub>4</sub> as an internal standard.

### Acknowledgements

We acknowledge financial support from the Lipid Research Fund and Research Grants Committee of the University of Hong Kong.

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