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# $^{13}C$ and $^{1}H$ NMR SPECTRA OF BIOLOGICALLY ACTIVE COMPOUNDS. VII. DIASTEREOMERS OF 2,2-DIALKYLSPIRO[CYCLOPROPANE-3,3'-INDENE]-1-CARBOXYLIC ACIDS OF THE PYRETHROID SERIES

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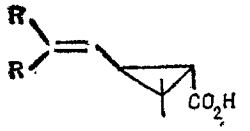
The structures have been established and the stereochemical assignments have been made of eight pairs of diastereomers and three quartets of stereoisomers of esters of 2,2-dialkylspiro[cyclopropane-3,3'-indene]-1-carboxylic acids of the pyrethroid series by the methods of $^{13}C$ NMR spectroscopy using the shift reagent $Eu(fod)_3$. Criteria have been found for assigning the stereoisomers on the basis of the characteristic values of the $^{13}C$ NMR chemical shifts of the signals of the methyl groups at C-2 for determining configuration of the substituents of the cyclopropane moiety of the molecule and of the C-2 signal itself for identifying isomers with respect to the side chain of the pyrethroid molecule. Criteria are proposed for identifying stereoisomers from the chemical shifts of the protons of the gem-dimethyl groups at C-2 in the $^{1}H$ NMR spectra.

In recent years, highly effective synthetic pyrethroids with a low toxicity for warm-blooded mammals that do not pollute the environment, consisting of esters of chrysanthemic (A) or permethric (B) acids, have found wide use in a system of protecting plants from harmful insects [1, 2]. Extremely promising pyrethroids are esters of 2,2-dimethylspiro-[cyclopropane-3,3'-indene]-1-carboxylic acid [3, 4].




R = Me(A)
R = Cl(B)

By $^{13}C$ NMR spectroscopy using the shift reagent $Eu(fod)_3$ and also by $^{1}H$ NMR we have shown the structures and have established the stereochemistry of isomers of a series of new synthesized derivatives of 2,2-dialkylspiro[cyclopropane-3,3'-indene]-1-carboxylic acid (I-XI).

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TABLE 1. Parameters of the $^{13}C$ NMR Spectra of the Stereoisomers of Compounds (I-XI) ($\delta$, ppm, $CDCl_3$, 25°C, 22.5 MHz)

| Atom | Ia* | $\Delta\delta_{Eu}$ | Ib* | $\Delta\delta_{Eu}$ | IIa | IIb |
|---|---|---|---|---|---|---|
| C-1 | 40,85 | 2,99 | 38,14 d | 2,85 | 41,12 d | 38,35 d |
| C-2 | 34,35 s | 2,52 | 32,13 s | 1,70 | 34,24 s | 31,97 s |
| C-3 | 49,36 s | 2,63 | 49,14 s | 1,93 | 49,20 s | 48,98 s |
| C-4 | 143,74 s | 0,82 | 140,98 s | 1,28 | 143,96 s | 141,14 s |
| C-5 | 144,44 s | 0,63 | 144,82 s | 0,78 | 144,56 s | 144,88 s |
| C-6 | 129,98 d | 0,90 | 130,30 d | 0,74 | 129,82 d | 130,14 d |
| C-7 | 135,40 d | 1,95 | 138,10 d | 0,62 | 135,67 d | 138,32 d |
| C-8 | 121,26 d | 0,65 | 125,05 d | 1,36 | 121,26 d | 125,10 d |
| C-9 | 123,86 d | 0,35 | 124,18 d | 0,67 | 123,86 d | 124,07 d |
| C-10 | 121,69 d | 0,28 | 121,58 d | 0,44 | 121,69 d | 121,52 d |
| C-11 | 126,24 d | 0,33 | 126,13 d | 0,47 | 126,18 d | 126,02 d |
| C-12 | 170,35 s | 2,61 | 169,10 s | 2,27 | 170,72 s | 169,42 s |
| C-13 | 23,46 q | 0,79 | 16,90 q | 1,62 | 23,57 q | 16,90 q |
| C-14 | 19,83 q | 2,07 | 27,25 q | 0,49 | 19,88 q | 27,36 q |
| C-15 | 65,94 m | 3,74 | 65,67 t | 2,82 | 60,52 t | 60,30 t |
| C-16 | 137,73 s | 0,67 | 137,70 s | 0,68 | 14,20 q | 14,20 q |
| C-17 | | | | | | |
| C-18 | | | | | | |
| C-19 | | | | | | |

| Atom | IIIa | IIIb | IVa | IVb | Va | Vb |
|---|---|---|---|---|---|---|
| C-1 | 40,26 d | 37,93 d | 40,34 d | 38,14 d | 43,45 d | 40,31 d |
| C-2 | 33,48 s | 31,37 s | 33,56 s | 31,56 s | 37,50 s | 34,51 s |
| C-3 | 48,11 s | 47,84 s | 47,98 s | 47,81 s | 48,76 s | 48,28 s |
| C-4 | 144,56 s | 141,68 s | 144,71 s | 142,22 s | 143,36 s | 140,81 s |
| C-5 | 145,74 s | 146,01 s | 145,07 s | 145,07 s | 140,50 s | 140,81 s |
| C-6 | 137,99 s | 138,10 s | 149,07 s | 149,18 d | 140,76 s | 140,81 s |
| C-7 | 130,25 d | 133,23 d | 127,05 d | 129,95 d | 147,16 d | 149,26 d |
| C-8 | 121,04 d | 124,88 d | 121,28 d | 125,24 d | 121,09 d | 124,56 d |
| C-9 | 123,86 d | 124,07 d | 123,73 d | 123,99 d | 124,08 d | 123,75 d |
| C-10 | 119,42 d | 119,14 d | 119,85 d | 119,55 d | 124,99 d | 125,16 d |
| C-11 | 126,08 d | 125,92 d | 125,94 | 125,75 d | 126,73 d | 126,51 d |
| C-12 | 170,88 s | 169,70 s | 170,88 s | 169,82 s | 170,13 s | 168,3 s |
| C-13 | 23,62 q | 16,96 q | 23,62 q | 16,98 q | 23,57 q | 17,07 q |
| C-14 | 19,78 q | 27,25 q | 19,83 q | 26,79 q | 19,99 q | 27,63 q |
| C-15 | 60,36 t | 60,14 t | 60,36 t | 60,22 t | 61,01 t | 60,68 t |
| C-16 | 14,20 q | 14,20 q | 14,28 q | 14,28 q | 14,25 q | 14,14 q |
| C-17 | 12,89 q | 13,17 q | 27,17 d | 27,28 d | 195,48 s | 195,05 s |
| C-18 | | | 21,86 q | 21,86 q | 27,63 d | 27,63 d |
| C-19 | | | 22,16 q | 22,16 q | | |

| Atom | VIa† | VIb† | VIIa† | VIIb† | VIIIa* | VIIIb* |
|---|---|---|---|---|---|---|
| C-1 | 42,59 d | 39,50 d | 42,59 d | 39,39 d | 40,04 d | 38,87 d |
| C-2 | 37,60 s | 34,57 s | 37,49 s | 34,57 s | 33,70 s | 31,70 s |
| C-3 | 48,98 s | 48,44 s | 48,92 s | 48,44 s | 48,11 s | 48,00 s |
| C-4 | 142,98 s | 140,27 s | 143,19 s | 140,54 s | 144,60 s | 142,00 s |
| C-5 | 140,48 s | 140,76 s | 140,71 s | 140,71 s | 144,82 s | 144,93 s |
| C-6 | 141,14 s | 141,09 s | 133,30 s | 133,61 s | 149,26 s | 149,26 s |
| C-7 | 146,23 d | 148,51 d | 145,86 d | 148,40 d | 126,73 d | 129,71 d |
| C-8 | 121,09 d | 123,86 d | 121,20 d | 124,40 d | 121,31 d | 125,16 d |
| C-9 | 124,18 d | 124,18 d | 123,10 d | 124,94 d | 123,75 d | 124,02 d |
| C-10 | 125,16 d | 125,16 d | 124,94 d | 122,88 d | 119,85 d | 119,58 d |
| C-11 | 126,94 d | 126,68 d | 126,83 d | 126,62 d | 125,97 d | 125,86 d |
| C-12 | 169,48 s | 167,58 s | 169,31 s | 167,80 s | 170,56 s | 169,42 s |
| C-13 | 23,46 q | 16,90 q | 23,46 q | 16,90 q | 23,51 q | 16,90 q |
| C-14 | 19,94 q | 27,47 q | 20,05 q | 27,47 q | 19,83 q | 26,71 q |
| C-15 | 53,53 t | 53,26 t | 53,21 t | 53,21 t | 65,76 t | 65,56 t |
| C-16 | | | | | 137,84 s | 137,84 s |
| C-17 | 195,54 s | 195,54 s | 164,06 s | 164,06 s | | |
| C-18 | 27,69 q | 27,69 q | 51,58 q | 51,58 q | | |
| C-26 | | | | | 27,14 d | 27,14 d |
| C-27 | | | | | 21,83 q | 21,83 q |
| C-28 | | | | | 22,11 q | 22,11 q |

TABLE 1 (continued)

| Atom | IXa* | IXb* | IXc* | IXd† |
|---|---|---|---|---|
| C-1 | 41,39 d | 37,60 d | 40,79 d | 38,85 d |
| C-2 | 40,20 s | 37,60 s | 40,58 s | 37,87 s |
| C-3 | 50,06 s | 49,25 s | 49,68 s | 49,41 s |
| C-4 | 144,01 s | 140,49 s | 144,17 s | 141,09 s |
| C-5 | 144,88 s | 144,82 s | 144,71 s | 145,26 s |
| C-6 | 130,36 d | 130,42 d | 130,25 d | 130,58 d |
| C-7 | 135,61 d | 137,78 d | 135,72 d | 138,39 d |
| C-8 | 121,85 d | 124,88 d | 121,36 d | 124,72 d |
| C-9 | 124,34 d | 124,02 d | 124,40 d | 124,34 d |
| C-10 | 121,96 d | 121,58 d | 121,96 d | 121,85 d |
| C-11 | 126,73 d | 126,13 d | 126,68 d | 126,45 d |
| C-12 | 170,26 s | 168,61 s | 170,18 s | 168,83 s |
| C-13 | 20,26 q | 13,38 q | 16,36 q | 23,68 q |
| C-14 | 26,17 t | 34,02 t | 29,80 t | 22,86 t |
| C-15 | 11,22 q | 10,78 q | 10,94 q | 10,94 q |
| C-16 | 53,64 t | 53,04 t | 53,80 t | 53,42 t |
| C-17 | | | | |
| C-18 | | | | |
| C-19 | | | | |

| Atom | Xa* | Xb* | Xc* | Xd* |
|---|---|---|---|---|
| C-1 | 41,45 d | 38,90 d | 40,80 d | 38,90 d |
| C-2 | 39,61 s | 38,04 s | 40,04 s | 37,38 s |
| C-3 | 49,52 s | 49,14 s | 49,20 s | 49,14 s |
| C-4 | 143,69 s | 140,76 s | 143,84 s | 140,87 s |
| C-5 | 144,44 s | 144,77 s | 144,39 s | 144,77 s |
| C-6 | 129,87 d | 130,20 d | 129,87 d | 130,20 d |
| C-7 | 135,40 d | 138,78 d | 135,50 d | 138,10 d |
| C-8 | 121,42 d | 125,10 d | 120,93 d | 124,83 d |
| C-9 | 123,86 d | 124,13 d | 123,97 d | 124,24 d |
| C-10 | 121,63 d | 121,47 d | 121,64 d | 121,47 d |
| C-11 | 126,24 d | 126,08 d | 126,24 d | 126,08 d |
| C-12 | 170,45 s | 169,10 s | 170,40 s | 169,10 s |
| C-13 | 20,21 q | 13,44 q | 16,25 q | 23,88 q |
| C-14 | 25,74 t | 34,02 t | 29,53 t | 22,34 t |
| C-15 | 11,11 q | 10,84 q | 10,84 q | 10,84 q |
| C-16 | 65,99 t | 65,61 t | 65,94 t | 65,67 t |
| C-17 | 137,78 s | 137,78 s | 137,78 s | 137,78 s |

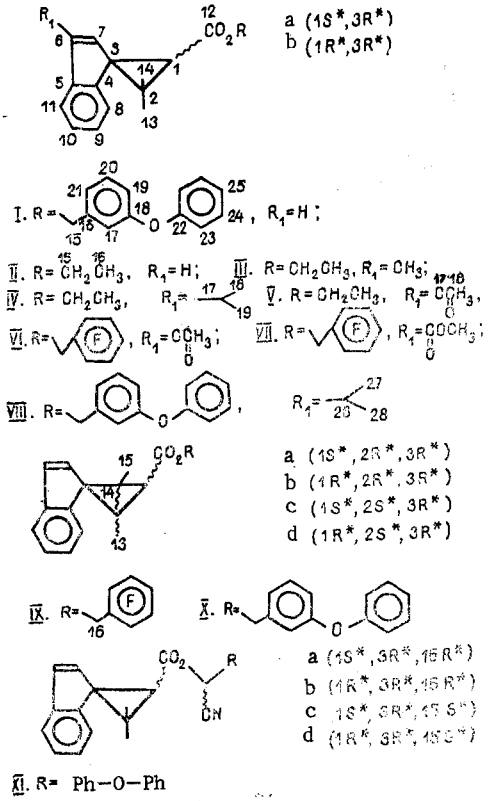
| Atom | XIa* | XIb* | XIc* | XId* |
|---|---|---|---|---|
| C-1 | 39,88 d | 37,08 d | 39,70 d | 37,14 d |
| C-2 | 35,25 s | 32,86 s | 34,86 s | 32,57 s |
| C-3 | 49,88 s | 49,74 s | 49,94 s | 49,81 s |
| C-4 | 143,22 s | 140,22 s | 143,15 s | 140,22 s |
| C-5 | 144,40 s | 144,78 s | 144,40 s | 144,85 s |
| C-6 | 130,75 d | 130,82 d | 130,82 d | 131,01 d |
| C-7 | 134,53 d | 137,41 d | 134,34 d | 137,28 d |
| C-8 | 121,35 d | 124,87 d | 121,29 d | 124,94 d |
| C-9 | 124,18 d | 124,02 d | 124,29 d | 124,48 d |
| C-10 | 121,87 d | 121,29 d | 121,83 d | 121,81 d |
| C-11 | 126,57 d | 126,57 d | 126,57 d | 126,51 d |
| C-12 | 168,87 s | 167,43 s | 168,81 s | 167,43 s |
| C-13 | 23,37 q | 16,71 d | 23,30 q | 16,78 q |
| C-14 | 19,78 q | 27,09 q | 19,71 q | 27,09 q |
| C-15 | 62,54 d | 62,47 d | 62,40 d | 62,21 d |
| C-16 | 116,06 s | 116,00 s | 115,93 s | 115,73 s |
| C-17 | 133,30 s | 133,56 s | 133,10 s | 133,69 s |
| C-18 | | | | |
| C-19 | | | | |

*C-17 118.33 d; C-18 157.45 s; C-19 118.33 d; C-20 129.82 d; C-21 122.72 d; C-22 156.80 s; C-23 118.98 d; C-24 129.71 d; C-25 123.37 d. For (Ib) and also for (VIII), (X), and (XI) the CSs of the phenoxyphenyl radical were close to those given above for compound (Ia).

†The signals of the aromatic ring were not observed in the spectrum because of intense splitting of the $^{19}F$ nuclei.

Table 1 gives the parameters of the $^{13}C$ NMR spectra in the form of chemical shifts (CSs) and multiplicities of the signals of the spiro[cyclopropaneindene]s studied (I-XI). The stereoisomers of the first pair of compounds (Ia) and (Ib) were separated by high performance liquid chromatography (HPLC) and the $^{1}H$ and $^{13}C$ NMR spectra were recorded both for the individual isomers and with the addition of the shift reagent $Eu(fod)_3$. The values of the additional CSs ($\Delta\delta_{Eu}$) are also given in Table 1.

The assignment of the signals and then stereochemical identification were performed on the basis of experiments with the addition of a shift reagent. For compound (I), the formation of only two stereoisomers with the anti- and syn-orientations of the ethoxycarbonyl group is characteristic, since the presence of the gem-dimethyl group leads to the degeneration of the chirality of one of the atoms of the cyclopropane ring. As was to be expected, the signals of the gem-dimethyl groups proved to be the most informative. The presence of two cis-interactions in isomer (Ia) for the C-14 methyl group leads to a diamagnetic shift of the signal in comparison with the signal of the C-13 methyl group. For it, a stronger, in comparison with C-13, induced CS caused by $Eu(fod)_3$ is observed because of its closeness to the carboxy group at which the coordination of the shift reagent takes place. The atoms of the C-7 double bond are present in the same semiplane, the signal of the C-7 atom also experiencing a considerable paramagnetic shift. Then the C-4 signals and those of the other aromatic carbon atoms of the indene fragment of the molecule experience only a slight shift as a result of the anti-orientation of the carboxy group.




In the isomer (Ib), conversely, the C-4 and C-8 signals have greater values of the induced CSs than the signal of C-7 at the double bond. The syn-orientation of the carboxy group cause a considerable screening of the C-13 methyl group, exceeding in value the effect for the isomer (Ia) because of the difference of the interactions with the double bond and the aromatic ring. The more than threefold greater values of the induced CSs for C-13 than for C-14 unambiguously show the assumed syn-orientation of the carboxy group in stereoisomer (Ib). It follows from this that in the $^{13}C$ NMR spectra the signals of the gem-dimethyl groups are stereochemically informative, and from the screening of their signals it is possible to assign isomers of type (I) to the syn (b) or anti (a) stereochemical series.

The parameters of the $^{1}H$ NMR spectra of the stereoisomeric pair (Ia, Ib) are given in Table 2. In the strong-field region two signals of protons of gem-dimethyl groups are observed. The single proton of the cyclopropane ring resonates in the form of a singlet at

TABLE 2. Parameters of the $^1H$ NMR Spectra of Stereoisomers of Compounds (I), (IX), and (X) ($\delta$, ppm, $J_{^1H-^1H}$, Hz, $CDCl_3$, 25°C, 100 MHz)

| Compound | H (C-1) | H (C-6) | H (C-7) | H (C-13) | H (C-14) | H (C-15) | H (C-16) | Ph |
|---|---|---|---|---|---|---|---|---|
| Ia | 2,72 s | 6,89—7,37 | 6,86 d (5,6) | 1,49 s | 1,59 s | 5,09 d 4,98 d (12,2) | | 6,89—7,37 m |
| Ib | 2,74 s | 6,86 d (5,6) | 6,22 d (5,6) | 1,68 s | 1,47 s | 5,09 d 4,91 d (12,3) | | 6,92—7,39 m |
| IXa | 2,66 s | 6,88 s | 6,88 s | 1,49 s | 2,00 q (7,1) | 0,89 t (7,1) | 5,16 d 5,30 d (12,0) | 7,18—7,41 m |
| IXb | 2,65 s | 6,86 d (5,6) | 6,22 d (5,6) | 1,67 s | mq (7,3) | 0,91 t (7,3) | 5,06 d 5,14 d (12,0) | 7,00—7,67 m |
| IXc | 2,68 s | 6,87 s | 6,87 s | 1,57 s | 1,96 mq (7,5) | 0,76 t (7,5) | 5,17 d 5,33 d (12,0) | 7,10—7,41 m |
| IXd | 2,70 s | 6,88 d (5,6) | 6,26 d (5,6) | 1,46 s | 2,29 q (7,3) | 0,77 t (7,3) | 5,11 d 5,33 d (12,0) | 7,18—7,41 m |
| Xa | 2,72 s | 6,81—7,40 m | 6,81—7,40 m | 1,50 s | 1,72—2,34 m | 0,88 t (7,3) | 4,98 d 5,14 d (13,4) | 4,81—4,80 m |
| Xb | 2,72 s | 6,83 d (5,6) | 6,22 d (5,6) | 1,66 s | 1,72—2,34 m | 0,90 t (7,3) | 4,91 d 5,08 d (12,6) | 7,83—7,75 m |
| Xc | 2,37 s | 6,81—7,40 m | 6,81—7,40 m | 1,58 s | 1,72—2,34 m | 0,77 t (7,3) | 5,04 d 5,09 d (12,2) | 6,81—7,40 m |
| Xd | 2,74 s | 6,85 d (5,6) | 6,24 d (5,6) | 1,46 s | 1,72—2,34 m | 0,79 t (7,3) | 4,93 d 5,04 d (12,4) | 6,83—7,75 m |

2.72 ppm (Ia) or 2.74 ppm (Ib). In the stereoisomer (Ia), the signals of the olefinic and aromatic protons overlap and are observed in the form of a complex multiplet at 6.98-7.38 ppm. Characteristic for the syn-isomer (Ib) is a diamagnetic shift of the signal of C-7 proton because of the $\gamma$-trans influence of the carboxy group through the cyclopropane ring in a similar way to what has been described previously. The spatial arrangement of the gem-dimethyl group has been established on the basis of the $\gamma$-effect of the carboxy group substituent: The signals of the protons of the cis-located methyl group are shifted downfield and those of the trans-methyl group upfield [5].

By using the criteria obtained it is not difficult to determine the composition of a mixture of the two diastereomers (IIa) and (IIb) from their $^{13}C$ NMR spectra and to establish the orientation of the ethoxycarbonyl group relative to the plane of the cyclopropane ring. Thus, the position of the C-13 signal in the stronger-field region (16.90 ppm) indicates the syn configuration of the ethoxycarbonyl group for (IIb), in contrast to the anti configuration for (IIa) ($\delta$ for C-13 = 19.88 ppm). The absence of signals of two aromatic rings in comparison with the spectra of compound (I) facilitates the assignment of the signals of the indene fragment of the molecule. The singlet C-4 singlet and the doublet C-7 signal can be used as additional characteristics in determining the orientation of the carboxy group.

The presence of a methyl group at C-6 in compound (III) leads to the appearance of additional singlet signals the values of the CSs of which confirm the assignment of the signals for the double bond [6]. Stereochemical assignments in a mixture of approximately equal amounts of the diastereomers are similar to the assignment of isomers (IIa) and (IIb) described previously.

The isomeric pair (IVa) and (IVb) in equal amounts was also identified from the signals of the gem-dimethyl groups. Interesting facts are the small changes in the CSs for the methine carbon atom on passing from one isomer to the other ($\Delta\delta$ for C-17 = 0.11 ppm) and the more appreciable differences for the diastereotopic C-18 and C-19 methyl groups relative to the C-3 chiral center. In order to confirm this assignment, isomer (IVb) was isolated in the individual form and, thus, the existence of diastereotopic effect for the gem-dimethyl groups of the isopropyl substituent was confirmed.

The acetate substituent at the double bond of each individual isomer (Va) and (Vb) shifts the informative C-7 doublet signal fairly powerfully downfield, which considerably facilitates spectral stereochemical assignments.

The presence of an ethyl group at C-2 leads to the appearance of a new chiral center and to the formation of four stereoisomers in the case of compound (IX). In actual fact, the spectrum of the reaction product corresponded to a set of four stereoisomers which were then isolated in the individual form, and the $^{13}C$ and $^{1}H$ NMR spectrum were recorded for each of them (Tables 1 and 2, respectively). Stereoisomers were identified from the signals of the C-13 methyl group. The signal was present in the strongest field for the 1-syn-2-anti isomer (IXb) having the greatest steric compression for the C-13 methyl group ($\delta$ for C-13 = 13.38 ppm). This was followed by the isomer (IXc) with the 1-anti-2-syn configuration of the substituents ($\delta$ for C-13 = 16.36 ppm), in which the methyl group participates in interaction with the C-7 double bond and with the carboxy group. Less hindered is the C-13 methyl group in the isomeric pair (IXa, IXd) differing by the interaction of this group with the aromatic ring [(IXa), $\delta$ for C-13 = 20.26 ppm] or with the double bond [(IXd), $\delta$ for C-13 = 23.88 ppm] of the indene moiety of the molecule. Also informative are the signals of the C-14 methylene group, the differences between which in the stereoisomers are up to 4 ppm.

Analogous features of the behavior of the signals as a function of the stereochemistry of the molecule are observed in the $^{1}H$ NMR spectra (see Table 2). On comparing the spectra of all the possible isomers (IXa-IXd), it was possible to establish the stereochemistry of each individual compound unambiguously. For isomers (IXa) and (IXc), each with an anti-carboxy group, the signals of the protons at the double bond resonate in the region of aromatic protons and were not identified, while the syn-oriented carboxy group in each of the isomers (IXb) and (IXd)causes diamagnetic shifts of the protons at C-7 (6.22 and 6.26 ppm, respectively) which form an AB system with the vicinal protons at C-6. The cis and trans positions of the methyl and ethyl groups at C-2 relative to the substituent at C-1 were established from the values of the CSs of the protons of the methyl group. The weak-field signal of the protons of the C-13 methyl group (1.67 ppm) in isomer (IXb) corresponds to the position of the signal of the protons at C-13 of isomer (Ib), while for isomer (IXd) a diamagnetic shift of the C-13 signal (1.46 ppm) is characteristic. The stereoisomeric pair (IXa) and (IXc) likewise are readily distinguished through the signals of the protons of the C-13 methyl group by analogy with isomers (Ia) and (Ib).

The stereoisomers (Xa-Xd) with a meta-phenoxybenzyl group were identified in a mixture from the characteristic signals of the C-13 carbon atom, as in the preceding case (IXa-IXd).

The presence of a chiral center in the side chain of the pyrethroid molecule, introduced, for example, by replacing one of the protons of the C-15 methylene group by a nitrile (CN) group, also leads to an increase in the number of stereoisomers. Thus, in compounds (XI) a set of four stereoisomers (a-d) is formed, two of which it was possible to isolate in the individual form (a and d), while two (b and c) were characterized as a mixture with one another.

It must be mentioned that the isomers with the syn configuration (XIb and d) and with the anti configuration (XIc and a) of the carboxy group are readily distinguished from one another on the basis of the characteristic signals of the gem-dimethyl groups. The differences in the orientation of the nitrile group are finer. In this case, the signal of the C-2 atom of the cyclopropane ring proved to be informative, its diamagnetic shift showing the 15S* configuration of the nitrile group in the isomers (XIc) and (XId) [1].

## EXPERIMENTAL

$^{13}C$ NMR spectra were recorded on a JEOL SX 90Q spectrometer (22.5 MHz) with broad-band and off-resonance suppression in relation to protons. The solvent was $CDCl_3$ and the internal standard TMS. The resolution of the ADC was 0.6 Hz. The samples with the shift reagent $Eu(fod)_3$ were prepared in a dry box.

$^{1}H$ NMR spectra were recorded on a Tesla BS 567 spectrometer (100 MHz) in the pulsed regime with subsequent Fourier transformation. The synthesis of the compounds investigated has been described in [7].

## SUMMARY

1. The structure has been established and the stereochemical assignment has been made of eight pairs of diastereomers and three quartets of stereoisomers of esters of 2,2-dialkylspiro[cyclopropane-3,3'-indene]-1-carboxylic acids of the pyrethroid series by $^{13}C$ NMR spectra using the shift reagent $Eu(fod)_3$.

2. Criteria have been found for assigning the stereoisomers from the characteristic values of the $^{13}C$ NMR chemical shifts of the signals of the methyl groups at C-2 in order to determine the configuration of the substituents of the cyclopropane moiety of the molecule and the signal of the C-2 atom itself for the identification of the isomers in the side chain of the pyrethroid molecule. Criteria are suggested for identifying stereoisomers from the chemical shifts of the protons of the methyl groups of C-2 in the $^1H$ NMR spectra.

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