SYNTHESIS OF FURTHER 9-OXA AND 10-OXA ANALOGUES OF ACYCLIC JUVENOIDS*

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A series of esters and amides of 9-oxa- and 10-oxa-2,4-alkadienoic acids has been prepared. The substances are analogues of the insect juvenile hormone.

The present paper relates to preparation** of some 9-oxa and 10-oxa analogues of the insect juvenile hormone, namely, esters and amides of 9-oxa-2,4-alkadienoic acids and 10-oxa-2,4-alkadienoic acids; some syntheses have been partly reported in patent applications[1-3].

As the starting material in the preparation of both analogue types, there have been used branched 5-oxa and 6-oxa alcohols (for their synthesis see an earlier paper[4]) and converted into the corresponding oxa aldehydes *I – V* by oxidation with chromium trioxide-pyridine in dichloromethane[5]. The oxa aldehydes *I – V* directly yielded the esters and amides of 9-oxa- and 10-oxa-2,4-alkadienoic acids by reaction with dialkyl 3-alkoxycarbonyl-2-methyl-2-propenephosphonates[6,7] or dialkyl 3-(N,N-diethylaminocarbonyl)-2-methyl-2-propenephosphonates. By the action of acetylmethylenetriphenylphosphorane[8,9], the oxa aldehydes were converted to the α,β-unsaturated oxa ketones *VI – VIII* which afforded esters and amides of 9-oxa- and 10-oxa-2,4-alkadienoic acids by reaction with ethoxycarbonylmethylenetriphenylphosphorane[10,11] and N,N-diethylaminocarbonylmethylenetriphenylphosphorane, resp.

The reaction of oxa aldehydes with dialkyl 3-alkoxycarbonyl-2-methyl-2-propenephosphonates was performed in 1,2-dimethoxyethane[12] in the presence of sodium hydride as the base, or, in dimethylformamide[13] in the presence of alkanolic sodium alkoxide. Two geometric isomers were obtained, namely, *trans, trans-* and *cis,trans*-2,4-dienoates. When the reaction was performed at elevated temperatures

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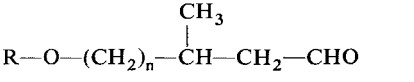
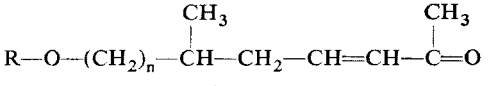
** The biological activity of the present substances will be reported elsewhere in collaboration with workers of the Institute of Entomology, Czechoslovak Academy of Sciences, Prague.

in dimethylformamide in the presence of sodium ethoxide, two additional compounds *XIIa,b* and *XVIIa* were formed and separated by chromatography. Their brutto formula was the same as that of the required 2,4-alkadienoates. In gas chromatography, two main peaks were observed. As finally established by analysis of NMR spectra, the by-products are double-bond-isomers, namely, a mixture of the 2,5- and 3,5-dienoate *XIIa,b* and the 3,5-dienoate *XVIIa*.

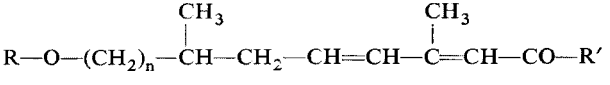
The oxa ketones *VI – VIII* obtained by reaction of oxa aldehydes with acetylmethylenetriphenylphosphorane contained mainly the *trans*-isomer. Reaction of the *trans*-isomer with ethoxycarbonylmethylenetriphenylphosphorane or N,N-diethylaminocarbonylmethylenetriphenylphosphorane afforded two isomers which were identical with those obtained by reaction of oxa aldehydes with dialkyl 3-ethoxy-



I, n = 1, R = $(CH_3)_2CHCH_2$—
II, n = 1, R = $(CH_3)_3CCH_2$—
III, n = 1, R = $(CH_3)_3C$—
IV, n = 2, R = $(CH_3)_3C$—
V, n = 2, R = $(C_2H_5)_2CH$—



VI, n = 1, R = $(CH_3)_3CCH_2$—
VII, n = 2, R = $(CH_3)_3C$—
VIII, n = 2, R = $(C_2H_5)_2CH$—



IX, n = 1, R = $(CH_3)_2CHCH_2$—, R′ = —OCH_3
X, n = 1, R = $(CH_3)_2CHCH_2$—, R′ = —OC_2H_5
XI, n = 1, R = $(CH_3)_2CHCH_2$—, R′ = —$N(C_2H_5)_2$
XII, n = 1, R = $(CH_3)_3CCH_2$—, R′ = —OC_2H_5
XIII, n = 1, R = $(CH_3)_3CCH_2$—, R′ = —$OCH(CH_3)_2$
XIV, n = 1, R = $(CH_3)_3CCH_2$—, R′ = —$N(C_2H_5)_2$
XV, n = 1, R = $(CH_3)_3C$—, R′ = —OCH_3
XVI, n = 2, R = $(CH_3)_3C$—, R′ = —OCH_3
XVII, n = 2, R = $(CH_3)_3C$—, R′ = —OC_2H_5
XVIII, n = 2, R = $(CH_3)_3C$—, R′ = —$OCH(CH_3)_2$
XIX, n = 2, R = $(CH_3)_3C$—, R′ = —$N(C_2H_5)_2$
XX, n = 2, R = $(C_2H_5)_2CH$—, R′ = —OC_2H_5
XXI, n = 2, R = $(C_2H_5)_2CH$—, R′ = —$OCH(CH_3)_2$
XXII, n = 2, R = $(C_2H_5)_2CH$—, R′ = —$N(C_2H_5)_2$

carbonyl-2-methyl-2-propenephosphonate or diethyl 3-(N,N-diethylaminocarbonyl)-2-methyl-2-propenephosphonate.

The reaction of α,β-unsaturated oxa ketones *VI* – *VIII* with diethyl ethoxycarbonylmethanephosphonate resulted mainly in the formation of tars. Polymerisation of α,β-unsaturated ketones[14] and pseudoionone[13] in this reaction has been observed earlier.

EXPERIMENTAL

The IR spectra were taken in tetrachloromethane. The NMR spectra were measured in deuteriochloroform; tetramethylsilane was used as internal standard; chemical shifts are given in δ (p.p.m.) and coupling contants in Hz. Column chromatography was performed on silica gel partially deactivated by 12% water. Gas chromatography was carried out on a Pye Argon Chromatograph apparatus with a radioactive ionisation detector.

Preparation of Oxa Aldehydes *I* – *V*

To a solution of dry pyridine (9·5 g) in dichloromethane (150 ml) there was added portionwise with stirring at 10–20°C over 5 min dry chromium trioxide (6·0 g). After 15–20 min, the appropriate oxa alcohol (0·01 mol) was added dropwise and the stirring was continued for 15–30 min. The reaction course was checked by thin-layer chromatography. When the alcohol disappeared from the reaction mixture, the supernatant was decanted from tars and processed as usual to afford the crude oxa aldehyde which was then distilled. Yields, 80–90%.

The following oxa aldehydes were prepared in this manner: 3,7-dimethyl-5-oxaoctanal (*I*; b.p. 115–123°C/11 Torr*), 3,7,7,-trimethyl-5-oxaoctanal (*II*; b.p. 120–125°C/18 Torr*), 3,6,6-trimethyl-5-oxaheptanal (*III*; b.p. 110–117°C/15 Torr*), 3,7,7-trimethyl-6-oxaoctanal (*IV*; b.p. 122–130°C/14 Torr*), and 7-ethyl-3-methyl-6-oxanonanal (*V*; b.p. 135–145°C/13 Torr*).

Preparation of Esters *XII*, *XIII*, *XVII*, *XVIII*, *XX*, and *XXI* as well as Amides *XI*, *XIV*, *XIX*, and *XXII*

To a suspension of sodium hydride (75 mg) in 1,2-dimethoxyethane (5–8 ml) there was added dropwise under nitrogen with stirring at 20°C dialkyl 3-alkoxycarbonyl-2-methyl-2-propenephosphonate or diethyl 3-(N,N-diethylaminocarbonyl)-2-methyl-2-propenephosphonate (3·3 mmol each). The mixture was stirred for 1 h, treated dropwise with the appropriate oxa aldehyde (3 mmol), and stirred for additional 1–2 h. The reaction course was checked by thin-layer chromatography. When the oxa aldehyde disappeared, the mixture was diluted with water (previously acidified with acetic acid) and extracted with light petroleum. The extracts were processed as usual to afford a crude product which was purified by chromatography on silica gel (30–50 parts by weight) with the use of 12 : 1 (esters) or 4 : 1 (amides) light petroleum–ether as eluants. Yields, 50–60%. Two peaks were obtained in gas chromatography. The ratio of the *cis*- to the *trans*-isomer was 1 : 1·5–2·0 (with esters) and 1 : 1 (with amides).

In this manner, the aldehyde *I* was converted to the N,N-diethylamide of 3,7,11-trimethyl-9-oxa-2,4-dodecadienoic acid (*XI*). The aldehyde *II* afforded ethyl 3,7,11,11-tetramethyl-9-oxa-2,4-dodecadienoate (*XII*), isopropyl 3,7,11,11-tetramethyl-9-oxa-2,4-dodecadienoate (*XIII*), and the N,N-diethylamide of 3,7,11,11-tetramethyl-9-oxa-2,4-dodecadienoic acid (*XIV*). From

* Bath temperature.

the aldehyde *IV*, there were obtained ethyl 3,7,11,11-tetramethyl-10-oxa-2,4-dodecadienoate (*XVII*), isopropyl 3,7,11,11-tetramethyl-10-oxa-2,4-dodecadienoate (*XVIII*), and the N,N-diethylamide of 3,7,11,11-tetramethyl-10-oxa-2,4-dodecadienoic acid (*XIX*). The aldehyde *V* yielded ethyl 11-ethyl-3,7-dimethyl-10-oxa-2,4-tridecadienoate (*XX*), isopropyl 11-ethyl-3,7-dimethyl-10-oxa-2,4-tridecadienoate (*XXI*), and the N,N,-diethylamide of 11-ethyl-3,7-dimethyl-10-oxa-2,4-tridecadienoic acid (*XXII*).

Preparation of Esters *IX*, *X*, *XII*, *XIIa,b*, *XV*, *XVI*, *XVII*, and *XVIIa*

To a stirred solution of dialkyl 3-alkoxycarbonyl-2-methyl-2-propenephosphonate (3·3 mmol) in dimethylformamide (5—8 ml) there was added dropwise under nitrogen at 20°C alkanolic sodium alkoxide (from 0·07 g of sodium and 0·7—1·4 ml of the appropriate alkanol). After 1 h, the corresponding oxa aldehyde (3·0 mmol) was added dropwise and the stirring was continued for 1—2 h at 20°C or at 120—130°C. The mixture was then processed analogously to the preceding preparation. Yields, 50—60%.

In this manner, (at 20°C), the aldehyde *I* afforded methyl and ethyl 3,7,11-trimethyl-9-oxa-2,4-dodecadienoate (*IX*, *X*) and the aldehyde *III* yielded methyl 3,7,10,10-tetramethyl-9-oxa-2,4-undecadienoate (*XV*). From the aldehyde *IV*, methyl 3,7,11,11-tetramethyl-10-oxa-2,4-dodecadienoate (*XVI*) and compound *XVII* were obtained.

Reaction of aldehydes *II* and *IV* (at 120—130°C) and chromatography of crude products on silica gel (50—70 parts by weight) from 12 : 1 light petroleum–ether afforded compounds *XII* and *XVII* in the first fractions of the effluent. The last chromatographic fractions from the reaction of the aldehyde *II* contained a mixture of ethyl 3,7,11,11-tetramethyl-9-oxa-3,5-dodecadienoate and ethyl 3,7,11,11-tetramethyl-9-oxa-2,5-dodecadienoate (*XIIa* and *XIIb*, resp.). The aldehyde *IV* yielded ethyl 3,7,11,11-tetramethyl-10-oxa-3,5-dodecadienoate (*XVIIa*).

Preparation of Unsaturated Oxa Ketones *VI*—*VIII*

A mixture of the appropriate oxa aldehyde (0·01 mol), acetylmethylenetriphenylphosphorane (4·0 g), and dry benzene (10—15 ml) was refluxed in the nitrogen atmosphere for 3 h; the benzene was removed by distillation and the viscous residue was repeatedly triturated with light petroleum. The extracts were combined, evaporated, the residual crude ketone distilled, and the distillate purified by chromatography on silica gel (50—70 parts by weight) with the use of 9 : 1 light petroleum–ether as eluant. Yields, 45—50%. When subjected to gas chromatography, the product exhibited two peaks in the ratio of 1 : 10—15. Subsequent experiments were performed with chromatographic fractions containing exclusively the principal product (*trans*-isomer).

In this manner, the aldehydes *II*, *IV*, and *V* yielded 6,10,10-trimethyl-8-oxa-3-undecen-2-one (*VI*), 6,10,10-trimethyl-9-oxa-3-undecen-2-one (*VII*), and 10-ethyl-6-methyl-9-oxa-3-dodecen-2-one (*VIII*).

Preparation of Esters *XII*, *XVII*, *XX* and Amides *XIV*, *XIX*, *XXII*

A mixture of the appropriate oxa ketone (1 mmol), ethoxycarbonylmethylenetriphenylphosphorane (400 mg) or N,N-diethylaminocarbonylmethylenetriphenylphosphorane (450 mg), benzoic acid (35 mg), and dry benzene (5 ml) was refluxed in the nitrogen atmosphere for 24 h. Further portions of the phosphorane (200 mg and 225 mg, resp.) and benzoic acid (17 mg) were then added and the whole mixture was refluxed for additional 16—20 h. The course of the reaction

TABLE I

Analyses and Boiling Points of Oxa Compounds *VI*—*XXII*

Compound	Formula m.w.	Calculated/Found % C	% H	% N	B.p.[a], °C Torr
VI	$C_{13}H_{24}O_2$ 212·3	73·54 73·89	11·39 11·55	—	140—145 13
VII	$C_{13}H_{24}O_2$ 212·3	73·54 73·55	11·39 11·45	—	140—148 13
VIII	$C_{14}H_{26}O_2$ 226·3	74·30 74·56	11·58 11·39	—	150—157 11
IX	$C_{15}H_{26}O_3$ 254·4	70·82 70·85	10·30 10·22	—	110—115 0·009
X	$C_{16}H_{28}O_3$ 268·4	71·60 71·67	10·51 10·35	—	110—120 0·009
XI	$C_{18}H_{33}NO_2$ 295·5	73·17 72·95	11·26 11·09	4·74 4·54	
XII	$C_{17}H_{30}O_3$ 282·4	72·30 72·24	10·71 10·47	—	110—120 0·009
XIIa,b	$C_{17}H_{30}O_3$ 282·4	72·30 72·44	10·71 10·43	—	105—115 0·008
XIII	$C_{18}H_{32}O_3$ 296·4	72·93 72·91	10·88 10·59	—	120—128 0·01
XIV	$C_{19}H_{35}NO_2$ 309·5	73·73 73·42	11·41 11·30	4·53 4·46	
XV	$C_{15}H_{26}O_3$ 254·4	70·82 70·94	10·30 10·17	—	105—115 0·009
XVI	$C_{16}H_{28}O_3$ 268·4	71·60 71·76	10·51 10·53	—	115—120 0·01
XVII	$C_{17}H_{30}O_3$ 282·4	72·30 72·02	10·71 10·73	—	115—120 0·009
XVIIa	$C_{17}H_{30}O_3$ 282·4	72·30 71·98	10·71 10·77	—	115—123 0·01
XVIII	$C_{18}H_{32}O_3$ 296·4	72·93 72·82	10·88 10·98	—	115—125 0·009
XIX	$C_{19}H_{35}NO_2$ 309·5	73·73 73·81	11·41 11·30	4·53 4·38	130—135 0·009
XX	$C_{18}H_{32}O_3$ 296·4	72·93 72·81	10·88 10·87	—	125—135 0·008

TABLE I
(*Continued*)

Compound	Formula m.w.	Calculated/Found % C	% H	% N	B.p.[a], °C Torr
XXI	$C_{19}H_{34}O_3$	73·50	11·04	—	130—135
	310·5	73·34	10·88		0·008
XXII	$C_{20}H_{37}NO_2$	74·25	11·53	4·33	
	323·5	74·25	11·43	4·40	

[a] Bath temperature.

was checked by thin-layer chromatography. The mixture was processed as usual to afford a crude product which was purified by chromatography on silica gel with the use of a 12 : 1 (with esters) or 4 : 1 (with amides) mixture of light petroleum and ether as the eluant. Yields, 50—60%. The ratio of the *cis*-isomer to the *trans*-isomer was 1 : 1.

By this procedure, the ketones *VI*, *VII*, and *VIII* were converted into the ethyl esters *XII*, *XVII*, and *XX* as well as the N,N-diethylamides *XIV*, *XIX*, and *XXII*.

Characteristics of Intermediates and Products

The structure of the title compounds (Table I) was confirmed by elemental analysis supplemented in some cases by analysis of IR and NMR spectra. The purity of substances and the ratio of isomers was determined by gas chromatography. The oxa ketones and esters of oxa acids were gas-chromatographed on Cellite impregnated with 10% Apiezon L at temperatures of 150°C (ketones) and 200—210°C (esters). The gas chromatography of oxa amides was performed on Gas Chrom impregnated with 3% SE-30 at temperature 175—185°C.

The IR spectra of oxa aldehydes *I*—*V* contained absorption bands indicating the presence of a —CHO group (1730, 2710, and 2800 cm^{-1}) and of an ethereal oxygen atom (1110 cm^{-1}). The IR spectra of unsaturated oxa ketones *VI*—*VIII* exhibited absorption bands of the $—COCH_3$ group in conjugation with a double bond (1680 and 1630 cm^{-1}) and of the ethereal oxygen atom (1110 cm^{-1}). The structure of *trans*-6,10,10-trimethyl-8-oxa-3-undecen-2-one (*VI*) was confirmed by the NMR spectrum: $C_{(10)}$ 3 × $—CH_3$ 0·92 (s); $C_{(6)}$ $—CH_3$ 0·94 (d), $J = 6·9$; $C_{(2)}$ $—CH_3$ 2·24 (s); 2 $H_{(5)}$ + $H_{(6)}$ 1·70—2·55 (m); 2 $H_{(9)}$ 3·04 (s); 2 $H_{(7)}$ 3·25 (m); $H_{(3)}$ 6·07 (m), $J_{(3,4)} = 15·5$, $J_{(3,5)} = 1·0$; $H_{(4)}$ 6·82 (m), $J_{(4,3)} = 15·5$, $J_{(4,5)} = 7·5$, $J_{(4,5')} = 7·0$.

The IR spectra of oxa acid esters *IX*, *XVI*, *XVII*, *XX*, and *XXI* exhibited absorption bands corresponding to an ester group conjugated with two double bonds (1710, 1640, 1610, 1240, and 1160 cm^{-1}) and an absorption band of the ethereal oxygen (1090 cm^{-1}). The structure of esters *X*, *XII*, and *XVII* was confirmed by NMR spectra; it was found that the products are mixtures of *trans*, *trans*- and *cis*, *trans*-isomers. Ethyl 3,7,11-trimethyl-9-oxa-2,4-dodecadienoate (X): $C_{(7)}$ + $C_{(11)}$ 3× $—CH_3$ 0·91 (d); 2 $H_{(6)}$ + H_7 + $H_{(11)}$ 1·6—2·4 (m); $C_{(3)}$—CH_3 1·98 (d) $J = 1·2$ (*cis*); $C_{(3)}$—CH_3 2·27 (d), $J = 1·2$ (*trans*); 2 $H_{(8)}$ + 2 $H_{(10)}$ 3·16 (m); $H_{(2)}$ 5·60 (bs), $J = 1·2$ (*cis*); $H_{(2)}$ 5·68 (bs), $J = 1·2$ (*trans*); $H_{(4)}$ + $H_{(5)}$ (*trans*) + $H_{(5)}$ (*cis*) 5·96—6·30 (compl.

multipl.); $H_{(4)}$ 7·60 (d), $J_{(4,5)} = 15·2$ (*cis*); $-COOC_2H_5$: $-CH_3$ 1·28 (t); $-CH_2-$ 4·18 (q). Ethyl 3,7,11,11-tetramethyl-9-oxa-2,4-dodecadienoate (*XII*): $C_{(11)}$ 3× $-CH_3$ 0·91 (s); $C_{(7)}-CH_3$ 0·93 (d); $C_{(3)}-CH_3$ 1·98 (d), $J = 1·2$ (*cis*); $C_{(3)}-CH_3$ 2·26 (d), $J = 1·05$ (*trans*); 2 $H_{(6)}$ 1·70 to 2·30 (m); 2 $H_{(10)}$ 3·30 (s); 2 $H_{(8)}$ 3·24 (m); $H_{(2)}$ 5·61 (d), $J = 1·2$ (*cis*); $H_{(2)}$ 5·69 (d), $J = 1·05$ (*trans*); $H_{(4)} + H_{(5)}$ (*trans*) + $H_{(5)}$ (*cis*) 5·90–6·30 (compl. multipl.); $H_{(4)}$ 7·58 (d), $J_{(4,5)} = 15·5$ (*cis*); $-COOC_2H_5$: $-CH_3$ 1·28 (t); $-CH_2-$ 4·17 (q). Ethyl 3,7,11,11-tetramethyl-10-oxa-2,4-dodecadienoate (*XVII*): $C_{(7)}-CH_3$ 0·89 (d), $J = 6·8$; $C_{(11)}$ 3× $-CH_3$ 1·18 (s); $C_{(3)}-CH_3$ 1·97 (d), $J = 1·5$ (cis); $C_{(3)}-CH_3$ 2·27 (d), $J = 1·2$ (*trans*); 2 $H_{(6)}$ + 2 $H_{(8)}$ 1·30–2·30 (m); 2 $H_{(9)}$ 3·37 (t); $H_{(2)}$ 5·59 (bs) (*cis*); $H_{(2)}$ 5·69 (bs) (*trans*); $H_{(4)} + H_{(5)}$ (*trans*) + $H_{(5)}$ (*cis*) 6·0–6·25 (compl. multipl.); $H_{(4)}$ 7·57 (d), $J_{(4,5)} = 16·1$ (*cis*); $-COOC_2H_5$: $-CH_3$ 1·27 (t); $-CH_2-$ 4·16 (q).

Composition of the mixture of compounds *XIIa,b* and structure of compound *XVIIa* was established by analysis of NMR spectra. The mixture of ethyl 3,7,11,11-tetramethyl-9-oxa-3,5-dodecadienoate (*XIIa*) and ethyl 3,7,11,11-tetramethyl-9-oxa-2,5-dodecadienoate (*XIVb*): $C_{(11)}$ 3× $-CH_3$ 0·90 (s); $C_{(7)}$ $-CH_3$ 1·02 (d), $J = 7·0$ (isomer b); $C_{(7)}$ $-CH_3$ 1·04 (d), $J = 6·8$ (isomer a); $C_{(3)}$ $-CH_3$ 1·82 (bs); $H_{(7)}$ 2·51 (m), 2 $H_{(10)}$ 3·04 (s); 2 $H_{(8)}$ 3·24 (m); $H_{(6)}$ 5·61 (dd), $J_{(6,7)} = 7·0$, $J_{(6,5)} = 15·4$ (isomer *a*); $H_{(4)}$ 5·88 (d), $J_{(4,5)} = 11·0$ (isomer *a*); $H_{(5)}$ 6·25 (m), $J_{(5,4)} = 11·0$, $J_{(5,6)} = 15·4$, $J_{(5,7)} = 1·0$ (isomer *a*); $H_{(2)}$ 6·36 (m) (isomer *b*); $-COOC_2H_5$: $-CH_3$ 1·25 (t); $-CH_2-$ 4·15 (q). Ethyl 3,7,11,11-tetramethyl-10-oxa-3,5-dodecadienoate (*XVIIa*; a mixture of *trans,trans-* and *cis, trans*-isomers): $C_{(7)}-CH_3$ 1·01 (d), $J = 6·6$; $C_{(11)}$ 3× $-CH_3$ 1·18 (s); 2 $H_{(8)}$ 1·53 (q); $C_{(3)}-CH_3$ 1·81 (bs) (*trans*); $C_{(3)}-CH_3$ 1·84 (bs) (*cis*); $H_{(7)}$ 2·35 (m), $J = 6·6$, $J_{(7,6)} = 7·6$; 2 $H_{(2)}$ 3·02 (s) (*trans*); 2 $H_{(2)}$ 3·14 (s) (*cis*); 2 $H_{(9)}$ 3·32 (t); $H_{(6)}$ 5·51 (dd), $J_{(5,6)} = 15·0$, $J_{(6,7)} = 7·6$; $H_{(4)}$ 5·88 (d), $J_{(4,5)} = 11·0$ (*trans*); $H_{(4)}$ 5·95 (d), $J_{(4,5)} = 11·0$ (*cis*); $H_{(5)}$ 6·23 (dd), $J_{(5,6)} = 15·0$, $J_{(4,5)} = 11·0$; $-COOC_2H_5$: $-CH_3$ 1·25 (t); $-CH_2-$ 4.15 (q).

The IR spectra of amides contained absorption bands which were assigned to a substituted amide group conjugated with two double bonds (1 630 and 1 600 cm^{-1}) and an ethereal oxygen atom (1 080 cm^{-1}). The NMR spectra confirmed structures of the amides *XIV*, *XIX*, and *XXII* and occurrence of *trans,trans-* and *cis,trans*-isomers. N,N-Diethylamide of 3,7,11,11-tetramethyl-9-oxa-2,4-dodecadienoic acid (*XIV*): $C_{(11)}$ 3× $-CH_3$ 0·91 (s); $C_{(7)}$ $-CH_3$ 0·90 (d); $C_{(3)}$ $-CH_3$ 1·83 (d), $J = 1·2$ (*cis*); $C_{(3)}$ $-CH_3$ 2·01 (d), $J = 1·1$ (*trans*); 2 $H_{(6)}$ + $H_{(7)}$ 1·7–2·04 (compl. multipl.) (*cis,trans*); 2 $H_{(10)}$ 3·02 (s); 2 $H_{(8)}$ 3·22 (m); $H_{(2)}$ 5·78 (bs) (*cis*); $H_{(2)}$ 5·88 (bs) (*trans*); $H_{(4)} + H_{(5)}$ (*trans*) + $H_{(5)}$ (*cis*) 5·80–6·20 (m); $H_{(4)}$ 6·82 (d), $J_{(4,5)} = 15·0$ (*cis*); $-C_2H_5$ (amide): 2× $-CH_3$ 1·15 (t); 2× $-CH_2-$ 3·38 (m). N,N-Diethylamide of 3,7,11,11-tetramethyl-10-oxa-2,4-dodecadienoic acid (*XIX*): $C_{(7)}-CH_3$ 0·89 (d), $J = 6·0$; 2× $-CH_3$ (ethyl) 1·17 (t); $C_{(11)}$ 3× $-CH_3$ 1·18 (s); $C_{(3)}-CH_3$ 1·94 (d), $J = 1·3$ (*cis*); $C_{(3)}$ $-CH_3$ 2·01 (d), $J = 1·1$ (*trans*); 2 $H_{(9)}$ + 2× $-CH_2-$ (ethyl) 3·35 (m); $H_{(2)}$ 5·77 (bs) (*cis*); $H_{(2)}$ 5·88 (bs) (*trans*); $H_{(5)}$ 5·91 (m); $H_{(4)}$ 6·80 (d), $J_{(4,5)} = 16·0$. N,N-Diethylamide of 11-ethyl-3,7-dimethyl-10-oxa-2,4-tridecadienoic acid (*XXII*): $C_{(12)} + C_{(11)}$ (ethyl) 2× $-CH_3$ 0·88 (t); $C_{(7)}-CH_3$ 0·90 (d), $J = 6·8$; 2× $-CH_3$ (amide) 1·14 (t); 2 $H_{(8)}$ + 2 $H_{(12)}$ + 2 H (ethyl) 1·3–1·7 (m); $C_{(3)}-CH_3$ 1·91 (m), $J = 1·2$ (*cis*); $C_{(3)}-CH_3$ 2·00 (m), $J = 1·05$ (*trans*); 2 $H_{(6)}$ 2·04 (m); $H_{(11)}$ 3·07 (m); $H_{(2)}$ 5·77 (m) (*cis*); H_2 5·87 (m) (*trans*); $H_{(4)} + H_{(5)}$ (*trans*) + $H_{(5)}$ (*cis*) 5·70–6·15 (compl. multipl.); $H_{(4)}$ 6·85 (d), $J_{(4,5)} = 15·0$ (*cis*).

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