SYNTHESIS OF SOME DIOXA ANALOGUES OF ACYCLIC JUVENOIDS*

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Esters and amides of aliphatic branched 5,10-, 6,9-, and 6,10- dioxaalkenoic and dioxaalkadienoic acids have been prepared as bioanalogues of the insect juvenile hormone. Some of them are active on *Hemiptera*, particularly on *Pyrrhocoridae*.

In continuation of our earlier work[1], some further dioxa analogues of the insect juvenile hormone have been prepared. The synthesis of some of these compounds has been partly published both in our[2] and foreign[3] patents and patent applications. The prepared esters and amides of 5,10-dioxaalkenoic, 5,10-dioxaalkadienoic, 5,10-dioxaalkatrienoic, 6,9-dioxaalkenoic, 6,9-dioxaalkadienoic, and 6,10-dioxaalkenoic acids (*X–XXIII*) are shown in on the opposite page and Table I.

In the preparation of analogues *X–XXIII*, the dioxa ketones *I–IX* were used as key intermediates. From the earlier prepared[4] 3,7-dimethyl-5-oxa-1-octanol (*Ia*) and 3,7,7-trimethyl-5-oxa-1-octanol (*IIIa*), the dioxa ketones *I* and *III* have been now prepared by reaction with diazoacetone[5] under catalysis of boron trifluoride etherate. The dioxa ketones *II* and *V* were obtained from the known[4] ethyl 3,7,7-trimethyl-5-oxa-2-octenoate and ethyl 3,6,6-trimethyl-5-oxa-2-heptenoate, resp. The lithium aluminium hydride reduction of these esters yielded the oxa alcohols *IIa* and *Va* which were converted to the required dioxa ketones *II* and *V* by an acid-catalysed reaction with diazoacetone. In the synthesis of the dioxa ketone *IV*, ethyl 2-methyl-2-butenoate was used as the starting material. The lithium aluminium hydride reduction of this ester gave 2-methyl-2-buten-1-ol which was converted to the oxa ketone *IVa* by reaction with 1-diazo-2-butanone in the presence of boron trifluoride etherate. The benzoic-acid-catalysed reaction[7] of the oxa ketone *IVa* with ethoxycarbonylmethylenetriphenylphosphorane[6] furnished the oxa ester *IVb* which was reduced with lithium aluminium hydride to the corresponding oxa alcohol *IVc*. Reaction of compound *IVc* with diazoacetone in the presence of boron trifluoride etherate afforded the dioxa ketone *IV*. In the preparation of the dioxa ketones *VI* to

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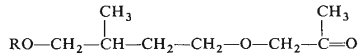
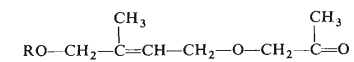
IX, 6-methyl-4-oxa-2-heptanone[4], 7-methyl-5-oxa-7-nonen-3-one, 6-methyl-5-oxa--2-heptanone[8], and 6,6-dimethyl-5-oxa-2-heptanone[8] were used as the starting material and converted to the corresponding oxa alcohols *VIa–IXa* by reduction with lithium aluminium hydride. Reaction of 3-buten-2-one with the oxa alcohols *VIa–IXa* in the presence of red mercuric oxide and boron trifluoride etherate afforded the dioxa ketones *VI–IX*.

Ia, R = $(CH_3)_2CHCH_2$
IIIa, R = $(CH_3)_3CCH_2$

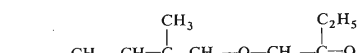


I, R = $(CH_3)_2CHCH_2$
III, R = $(CH_3)_3CCH_2$

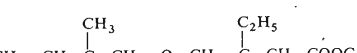
IIa, R = $(CH_3)_3CCH_2$
Va, R = $(CH_3)_3C$



II, R = $(CH_3)_3CCH_2$
V, R = $(CH_3)_3C$

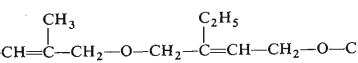


IVa

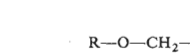


IVb

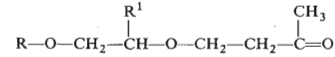
IVc



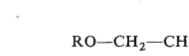
IV



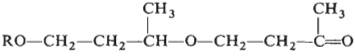
VIa, R = $(CH_3)_2CHCH_2$, $R^1 = CH_3$
VIIa, R = $CH_3CH{=}CCH_2$ (with CH_3), $R^1 = C_2H_5$



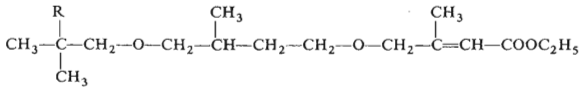
VI, R = $(CH_3)_2CHCH_2$, $R^1 = CH_3$
VII, R = $CH_3CH{=}CCH_2$ (with CH_3), $R^1 = C_2H_5$



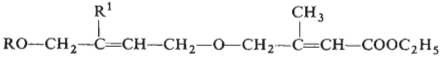
VIIIa, R = $(CH_3)_2CH$
IXa, R = $(CH_3)_3C$



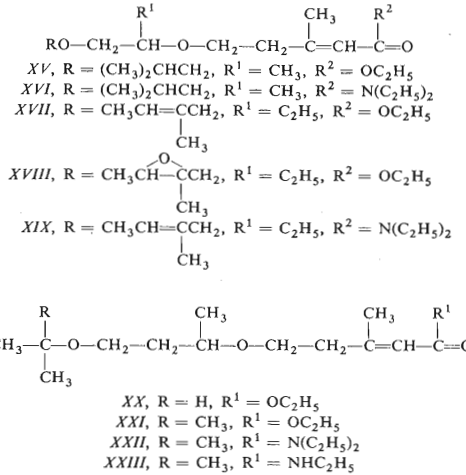
VIII, R = $(CH_3)_2CH$
IX, R = $(CH_3)_3C$



X, R = H
XII, R = CH_3



XI, R = $(CH_3)_3CCH_2$, $R^1 = CH_3$
XIII, R = $CH_3CH{=}CCH_2$ (with CH_3), $R^1 = C_2H_5$
XIV, R = $(CH_3)_3C$, $R^1 = CH_3$



SCHEME 1

The ethyl esters *X*–*XV*, *XVII*, *XX*, and *XXI* were prepared by the Wittig reaction of the dioxa ketones *I*–*IX* with ethoxycarbonylmethylenetriphenylphosphorane. The N,N-diethylamides *XVI*, *XIX*, and *XXII* were prepared from the ester *XV*, *XVII*, and *XXI* by saponification to acids, conversion of the acids to acyl chlorides by the action of thionyl chloride in the presence of pyridine[9], and reaction of the acyl chlorides with diethylamine. The N-ethylamide *XXIII* was prepared from the dioxa ketone *IX* by the modified[10] Wittig reaction with diethyl N-ethylaminocarbonylmethanephosphonate. The epoxy compound *XVIII* was prepared by epoxidation of the ester *XVII* with perphthalic acid.

EXPERIMENTAL

The IR spectra were taken in tetrachloromethane. The ^{1}H-NMR spectra were measured in deuteriochloroform with the use of tetramethylsilane as internal standard; chemical shifts are expressed in the δ scale (ppm) and the coupling constant J are given in Hz. Column chromatography was performed on the Pitra macroporous silica gel (produced by Service Laboratories of this Institute) partially deactivated with water (12%). Gas chromatography was performed on the Pye Argon Chromatograph (radioactive ionisation detection).

TABLE I

Analyses and Boiling Point[a] Data of Compounds *I*—*XXIII*

Compound	Formula (m.w.)	Calculated/Found		Distils at °C/Torr[a]
		% C	% H	
I	$C_{12}H_{24}O_3$	66·63	11·18	140—150
	(216·3)	66·42	10·98	15
II	$C_{13}H_{24}O_3$	68·39	10·60	150—155
	(228·3)	68·22	10·68	14
III	$C_{13}H_{26}O_3$	67·79	11·38	140—150
	(230·3)	67·58	11·20	14
IV	$C_{14}H_{24}O_3$	69·97	10·07	110—125
	(240·3)	69·81	9·96	0·1
V	$C_{12}H_{22}O_3$	67·25	10·35	135—140
	(214·3)	67·01	10·08	13
VI	$C_{11}H_{22}O_3$	65·30	10·96	130—135
	(202·3)	65·58	10·98	12
VII	$C_{13}H_{24}O_3$	68·39	10·60	155—165
	(228·3)	68·51	10·52	11
VIII[b]	$C_{11}H_{22}O_3$	65·30	10·96	125—130
	(202·3)	65·15	10·76	11
IX	$C_{12}H_{24}O_3$	66·63	11·18	130—140
	(216·3)	66·98	11·18	12
X	$C_{16}H_{30}O_4$	67·09	10·56	115—125
	(286·4)	66·90	10·48	0·01
XI	$C_{17}H_{30}O_4$	68·42	10·13	120—130
	(298·4)	68·22	10·34	0·009
XII	$C_{17}H_{32}O_4$	67·96	10·74	110—120
	(300·4)	68·11	10·71	0·009
XIII	$C_{18}H_{30}O_4$	69·64	9·74	145—150
	(310·4)	69·32	9·74	0·01
XIV	$C_{16}H_{28}O_4$	67·57	9·92	125—130
	(284·4)	67·24	9·76	0·009
XV	$C_{15}H_{28}O_4$	66·14	10·36	120—125
	(272·4)	66·41	10·34	0·01
XVI	$C_{17}H_{33}NO_3$[c]	68·19	11·11	145—150
	(299·4)	68·07	11·00	0·1
XVII	$C_{17}H_{30}O_4$	68·42	10·13	120—130
	(298·4)	68·74	9·95	0·009

TABLE I
(*Continued*)

Compound	Formula (m.w.)	Calculated/Found % C	Calculated/Found % H	Distils at °C/Torr[a]
XVIII	$C_{17}H_{30}O_5$ (314·4)	64·94 65·18	9·62 9·52	130—135 0·009
XIX	$C_{19}H_{35}NO_3$[d] (325·5)	70·11 69·85	10·84 10·58	140—155 0·009
XX[e]	$C_{15}H_{28}O_4$ (272·4)	66·14 66·48	10·36 10·41	95—105 0·009
XXI	$C_{16}H_{30}O_4$ (286·4)	67·09 67·33	10·56 10·43	95—105 0·009
XXII	$C_{18}H_{35}NO_3$[f] (313·5)	68·96 68·95	11·25 11·41	135—140 0·009
XXIII	$C_{16}H_{31}NO_3$[g] (285·4)	67·33 66·98	10·95 11·01	150—158 0·009

[a] The data refer to the bath temperature. [b] This substance has been reported earlier[3]. [c] Calculated: 4·69% N; found 4·48% N. [d] Calculated: 4·30% N; found: 4·27% N. [e] For the preparation of the methyl ester see ref.[3] [f] Calculated: 4·47% N; found: 4·24% N. [g] Calculated: 4·91% N; found: 4·97% N.

Oxa Alcohols *IIa*, *IVc*, *Va*—*IXa*

The appropriate unsaturated oxa ester (0·02 mol; at −15°C) or the corresponding oxa ketone (0·04 mol; at 20°C) was added dropwise to a suspension of lithium aluminium hydride (0·55 g) in ether (50 ml). The mixture was stirred at room temperature for 1 h and then refluxed for 30 min. The excess reagent was decomposed by the addition of water and hydrochloric acid and the ethereal layer processed as usual. The thus-obtained oxa alcohols were distilled under diminished pressure at the bath temperature given in parentheses and used in the next reaction. The yields were 82—87% (from esters) and 89—92% (from ketones). The following oxa alcohols were prepared: 3,7,7-trimethyl-5-oxa-2-octen-1-ol (*IIa*; 130—140°C at 12 Torr), 2-methyl-2-buten-1-ol (68 to 70°C at 30 Torr), 3-ethyl-7-methyl-5-oxa-2,7-nonadien-1-ol (*IVc*; 145—155°C at 12 Torr), 3,6,6-trimethyl-5-oxa-2-hepten-1-ol (*Va*; 105—115°C at 13 Torr), 6-methyl-4-oxa-2-heptanol (*VIa*; 105—110°C at 45 Torr), 7-methyl-5-oxa-7-nonen-3-ol (*VIIa*; 105—110°C at 10 Torr), 6-methyl-5-oxa-2-heptanol (*VIIIa*; 125—130°C at 60 Torr), and 6,6-dimethyl-5-oxa-2-heptanol (*IXa*; 105—110°C at 35 Torr).

Oxa Ketone *IVa* and Dioxa Ketones *I*—*V*

A solution of diazomethane (8·1 g) in ether (300 ml) was treated dropwise at −15°C under shaking with acetyl chloride (5·2 g; in the preparation of dioxa ketones *I*—*V*) or propionyl

chloride (6·1 g; in the preparation of the oxa ketone *IVa*). The mixture was kept with cooling for 1 h and then concentrated under diminished pressure at the temperature from −5°C to 0°C to the volume of 30−40 ml. The appropriate alcohol or oxa alcohol (0·1−0·15 mol) and boron trifluoride etherate (0·2−0·3 g) were added to the concentrate and the mixture heated to 20°C. When the evolution of nitrogen ceased, the mixture was washed with aqueous sodium hydrogen carbonate and processed as usual. Fractional distillation of the residue yielded a ketonic fraction which was purified by chromatography on silica gel (30 parts by weight). Light petroleum–diethyl ether (14 : 1 in the case of compound *IVa* and 7 : 1 in the case of dioxa ketones *I*−*V*) was used as eluant. Yields, 20−35%. In this manner, the following compounds were prepared: 7-methyl-5-oxa-7-nonen-3-one (*IVa*; b.p. 95−105°C at 13 Torr), 7,11-dimethyl-4,9-dioxa--2-dodecanone (*I*); 7,11,11-trimethyl-4,9-dioxa-6-dodecen-2-one (*II*), 7,11,11-trimethyl-4,9-dioxa--2-dodecanone (*III*), 7-ethyl-11-methyl-4,9-dioxa-6,11-tridecadien-2-one (*IV*), and 7,10,10-trimethyl-4,9-dioxa-6-undecen-2-one (*V*).

Dioxa Ketones *VI*−*IX*

A mixture of the appropriate oxa alcohol (0·3 ml), red mercuric oxide (0·05 g), and boron trifluoride etherate (0·05 g) was heated to 100−120°C for 10 min, cooled down, and added to a mixture of the oxa alcohol (total 0·04 mol) and 3-buten-2-one (3·0 g). The reaction mixture was kept at room temperature for 2−4 days and the course of the reaction checked by thin-layer chromatography. When the composition did not change, the mixture was poured into water and the product isolated. Fractional distillation yielded a ketonic fraction which was purified by chromatography on silica gel (30 parts by weight). Light petroleum–diethyl ether (7 : 1) was used as eluant. Yield, 35−45%. In this manner, the following compounds were prepared: 6,10-dimethyl-5,8-dioxa--2-undecanone (*VI*), 6-ethyl-10-methyl-5,8-dioxa-10-dodecen-2-one (*VII*), 6,10-dimethyl-5,9--dioxa-2-undecanone (*VIII*), and 6,10,10-trimethyl-5,9-dioxa-2-undecanone (*IX*).

Ethyl Esters *IVb*, *X*−*XV*, *XVII*, *XX*, and *XXI*

A mixture of the appropriate oxa ketone or dioxa ketone (5 mmol), ethoxycarbonylmethylenetriphenylphosphorane (2 g), benzoic acid (0·1 g), and benzene (20−30 ml) was refluxed under nitrogen for 18 h and processed as given below (preparation of compounds *IVb*, *XI*, *XII*, *XIII*, and *XIV*). In the preparation of esters *XV*, *XVII*, *XX*, and *XXI*, additional phosphorane (0·5 g) and additional benzoic acid (0·05 g) were introduced and the reflux continued for 18−24 h more. The course of the reaction was checked by thin-layer chromatography. When the starting ketone was no longer present, the benzene was evaporated and the residue extracted by repeated triturations with light petroleum. The extracts were pooled and processed as usual. The crude esters were purified by chromatography on silica gel with the use of light petroleum–diethyl ethers (9 : 1) as eluant. The head chromatographical fractions yielded the *cis*-isomer and the final fractions afforded the *trans*-isomer. The ratio of *cis*/*trans* isomers was 1 : 1·5 to 2·0, the yields were 60−75%. In this manner, the following esters were prepared: ethyl 3-ethyl-7-methyl-5-oxa--2,7-nonadienoate (*IVb*; b.p. 150−155°C at 15 Torr), ethyl, 3,8,12-trimethyl-5,10-dioxa-2-tridecenoate (*X*), ethyl 3,8,12,12-tetramethyl-5,10-dioxa-2,7-tridecadienoate (*XI*), ethyl 3,8,12,12-tetramethyl-5,10-dioxa-2-tridecenoate (*XII*), ethyl 8-ethyl-3,12-dimethyl-5,10-dioxa-2,7,12-tetradecatrienoate (*XIII*), ethyl 3,8,11,11-tetramethyl-5,10-dioxa-2,7-dodecadienoate (*XIV*), ethyl 3,7,11-trimethyl-6,9-dioxa-2-dodecenoate (*XV*), ethyl 7-ethyl-3,11-dimethyl-6,9-dioxa-2,11-tridecadienoate (*XVII*), ethyl 3,7,11-trimethyl-6,10-dioxa-2-dodecenoate (*XX*), and ethyl 3,7,11,11-tetramethyl-6,10-dioxa-2-dodecenoate (*XXI*).

N,N-Diethylamides *XVI*, *XIX*, and *XXII*

A mixture of the appropriate ethyl ester (1·05 mmol) and 1% ethanolic sodium hydroxide (10 ml) was kept at 20°C for 16 h and refluxed for 30 min. A portion of the ethanol was evaporated, the residual mixture diluted with water, and processed as usual to afford about 1 mmol of the corresponding acid.

A mixture of the appropriate dioxa acid (1 mmol), pyridine (0·1 g), and benzene (5 ml) was cooled down and treated with thionyl chloride (119 mg). The whole was kept at 20°C for 2 h, cooled down, and treated with a solution of diethylamine (160 mg) in benzene (2 ml). The whole mixture was kept at room temperature for 4—8 h, poured into water, extracted with ether, and the extracts processed as usual to afford the crude amide which was purified by chromatography on silica gel (30 to 50 parts by weight) with the use of light petroleum-diethyl ether (4 : 1) as eluant. The *cis* and *trans* isomers were partially separated by this procedure. Yields, 40—55%. In this manner, the following compounds were prepared: N,N-diethylamide of 3,7,11-trimethyl--6,9-dioxa-2-dodecenoic acid (*XVI*), N,N-diethylamide of 7-ethyl-3,11-dimethyl-6,9-dioxa--2,11-tridecadienoic acid (*XIX*), and N,N-diethylamide of 3,7,11,11-tetramethyl-6,10-dioxa--2-dodecenoic acid (*XXII*).

N-Ethylamide *XXIII*

Diethyl N-ethylaminocarbonylmethanephosphonate (400 mg) was added dropwise at 20°C under nitrogen to a suspension of sodium hydride (40 mg) in 1,2-dimethoxyethane (8 ml) and the mixture stirred for 1 h. 6,10,10-Trimethyl-5,9-dioxa-2-undecanone (300 mg) was then added and the whole stirred at 20—30°C for 5 h. The mixture was then poured into water and processed as usual to afford the crude amide which was purified by chromatography on silica gel (30 parts by weight) with the use of light petroleum–diethyl ether (7 : 3) as eluant. Yield, 200 mg of the pure N-ethylamide of 3,7,11,11-tetramethyl-6,10-dioxa-2-dodecenoic acid (*XXIII*).

Epoxy Ester *XVIII*

Ethereal perphthalic acid (68 mg in 0·5 ml) was added to a solution of ethyl 7-ethyl-3,11-dimethyl--6,9-dioxa-2,11-tridecadienoate (97 mg) in ether (2 ml) and the mixture kept at 0°C for 12 h. The crude product was chromatographed on neutral alumina (Reanal, Budapest, Hungary) of Brockmann activity II (5 g) with the use of light petroleum–diethyl ether (17 : 3) as eluant. Yield, 75 mg of ethyl 11,12-epoxy-7-ethyl-3,11-dimethyl-6,9-dioxa-2-tridecenoate (*XVIII*).

Characterisation of Substances

The substances *I*—*XXIII* were characterised by elemental analysis, IR spectra, and in some cases, by ^{1}H-NMR spectra. The purity and the *cis*/*trans* ratio was checked by gas chromatography. The dioxa ketones *I*—*IX* and the esters of dioxaalkenoic acids were chromatographed at 135 to 150°C and 195—200°C on Cellit impregnated by 10% of Apiezon L. The amides of dioxaalkenoic acids were chromatographed at 175°C on Gas Chrom Q impregnated by 3% of SE-30.

The IR spectra of the dioxa ketones *I*, *II*, *VI*—*IX* exhibited absorption bands of a methyl ketone at about 1720 and 1360 cm^{-1} and absorption bands of ethereal oxygen (1115—1120, 1080 cm^{-1}), the intensity of which was indicative of the presence of two ethereal oxygens in the molecule.

The structure of 7-methyl-5-oxa-7-nonen-3-one (*IVa*) was evidenced by ^{1}H-NMR spectra: H-1 0·995 (t, 3 H) $J = 8{\cdot}0$; $C_{(7)}$—CH_3 + $C_{(8)}$—CH_3 1·595 (s, 6 H); H-2 2·44 (q, 2 H), $J = 8{\cdot}0$; H-6 3·85 (bs, 2 H); H-4 3·90 (s, 2 H); H-8 5·46 (m, 1 H).

The IR spectra of esters of dioxaalkenoic acids *X*—*XV*, *XVII*, *XX*, and *XXI* exhibited absorption bands attributable to an ester group in conjugation with a double bond (at about 1 720, 1 660, 1 220, and 1 150 cm^{-1}) and absorption bands of the ethereal oxygen at about 1 110 and 1 080 cm^{-1}.

Structures of compounds *X*, *XV*, *XVII*, and *XX* were confirmed by ^{1}H-NMR spectra. Ethyl 3,8,12-trimethyl-5,10-dioxa-2-tridecenoate (*X*): $C_{(12)}$ 2 × —CH_3 0·890 (d, 6 H) $J = 6$; $C_{(8)}$—CH_3 0·930 (d, 3 H) $J = 6{\cdot}3$; H-7, H-8, H-12 1·4—2·0 (m, 4 H); $C_{(3)}$—CH_3 2·095 (d, 3 H) $J \sim 1$; H-9, H-12, 3·155 (d, 2 H) $J = 7{\cdot}0$; 3·24 (dd, 2 H) $J = 6{\cdot}5$, $J \leqq 1{\cdot}0$; H-6 3·50 (t, 2 H) $J = 6{\cdot}5$; H-4 3·92 (mt, 2 H); H-2 5·93 (mt, 1 H); —$COOC_2H_5$: —CH_3 1·275 (t, 3 H) $J = 7$; —CH_2— 4·16 (q, 2 H) $J = 7$. Ethyl 3,7,11-trimethyl-6,9-dioxa-2-dodecenoate (*XV*): $C_{(11)}$ 2 × —CH_3 0·87 (d, 6 H) $J = 6{\cdot}5$; $C_{(7)}$—CH_3 1·12 (d, 3 H) $J = 6{\cdot}0$; H-11 1·88 (mt, 1 H); $C_{(3)}$—CH_3 1·93 (d) $J = 1{\cdot}5$; 2·17 (d) $J = 1{\cdot}8$ (3 H); H-4 2·38 (t) $J = 7$; 2·87 (t) $J = 7$ (2 H); H-10 3·18 (d, 2 H) $J = 6{\cdot}5$; H-8 3·35 (t, 2 H) $J = 6{\cdot}0$; H-7 3·60 (mt, 1 H); H-5 3·67 (t, 2 H) $J = 7{\cdot}0$; H-2 5·72 (mt, 1 H); —$COOC_2H_5$: —CH_3 1·15 (t, 3 H) $J = 7$; —CH_2— 4·12 (q, 2 H) $J = 7$. Ethyl 7-ethyl-3,11-dimethyl-6,9-dioxa-2,11-tridecadienoate (*XVII*): $C_{(7)}$—CH_3 (ethyl) 0·89 (t, 3 H) $J = 7$; —CH_2— (ethyl) 1·40—1·60 (mt, 2 H); $C_{(12)}$—CH_3 1·60 (d, 3 H) $J = 5$; $C_{(11)}$—CH_3 1·62 (bs, 3 H); $C_{(3)}$—CH_3 1·94 (d) $J = 1{\cdot}3$; 2·2 (d) $J = 1{\cdot}5$ (3 H); H-4 2·39 (t) $J = 6$; 2·88 (t) $J = 6{\cdot}5$ (2 H); H-5, H-7, H-8 3·33 (mt) 3·55—3·80 (mt) (5 H); H-10 3·84 (mt, 2 H); H-12 5·46 (bm, 1 H); H-2 5·70 (mt, 1 H); —$COOC_2H_5$: —CH_3 1·25 (t, 3 H) $J = 7{\cdot}5$; —CH_2— 4·125 (q, 2 H) $J = 7{\cdot}5$. Ethyl 3,7,11-trimethyl-6,10-dioxa-2-dodecenoate (*XX*): $C_{(11)}$ 2 × —CH_3 1·11 (d, 6 H) $J = 6{\cdot}0$; H-8 1·68 (mt, 2 H); $C_{(3)}$—CH_3 1·93 (d) $J = 1{\cdot}2$; 2·175 (d) $J = 1{\cdot}4$ (3 H); H-4 2·27 (t) $J = 6{\cdot}5$; 2·27 (t) $J = 6$ (2 H); H-5, H-7, H-9, H-11 3·28—3·65 (mt, 6 H); H-2 5·61 (mt, 1 H); —$COOC_2H_5$: —CH_3 1·25 (t, 3 H) $J = 7$; —CH_2— 4·04 (q, 2 H) $J = 7$.

Biological Activity

The insect juvenile activity was expressed in ID-50 Morph. units indicating such an amount of the test substance in microgrammes per specimen which, when applied topically to the last instar larva causes the formation of a half-imaginal species. The esters of dioxa acids were active on *Dysdercus cingulatus* (0·05—500 Morph. units) and *Graphosoma italicum* (10—500 Morph. units), and feebly active on *Tenebrio molitor* (10—1 000 Morph. units) when compared with the amides *XXII* and *XXIII* (1·0—0·5 Morph. units). For details see ref.[11].

Elemental analyses were performed in the Analytical Department (Dr J. Horáček, Head) of this Institute by Mrs V. Rusová, Mrs A. Froňková, and Mrs Y. Černá. The IR spectra were measured by Mr P. Formánek and Mrs K. Matoušková, and interpreted by Dr J. Smolíková. The ^{1}H-NMR *spectra were measured and interpreted by Dr M. Masojídková and Dr P. Sedmera. The technical assistance was provided by Mrs A. Červenclová and Miss M. Tesaříková. Biological assays were carried out by Dr K. Sláma, Institute of Entomology, Czechoslovak Academy of Sciences, Prague.*

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