TERPENOID DERIVATIVES OF 4-HYDROXYPROPIOPHENONE AS JUVENOIDS AND JUVENOGENS. II.

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Received November 4th, 1980

A series of potential juvenoids and juvenogens was prepared by modifying the structure of 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone and 4-(3,7-dimethyl-2-octenyloxy)propiophenone.

In our last paper[1] we described juvenoids and juvenogens containing an alkoxy group in their molecules. Among other reactions used, modifying the primary structure of 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone and 4-(3,7-dimethyl-2-octenyloxy)propiophenone[1], which lead to the preparation of substances with juvenoid and juvenogenic activity in insect metabolism, the oxidation of the two mentioned compounds, as well as their derivatives *I–XIII* and *XV* (Table I), with monoperphthalic acid, was important from the point of view of final products, analogous to the intermediates of microsomal oxidation of unsaturated compounds in the insect organism.

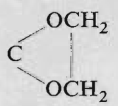
On reaction of these substances with an equivalent amount of peracid at room temperature we obtained predominantly monoepoxy derivatives in the case of diene compounds, containing the oxirane ring in the terminal part of the terpenoid chain (the mass ratio to diepoxy derivatives was about 12 : 1), while when two equivalents of the monoperphthalic acid were used, diepoxy compounds were obtained as the main products, in a 8 : 1 ratio with respect to the monoepoxy derivatives. Compounds *XXI* till *XXVIII* represent juvenogenic compounds from which active components are formed in the insect organism under the effect of carboxyl esterases.

The synthesis of oxirane derivatives was followed by other reactions, also leading to physiologically active substances (Table II). Thus compound *XVI* reacted with hydroxylamine in 96% ethanol under formation of oxime *XXXI* which was then converted on reaction with ethyl bromoacetate in the presence of NaH to O-ethoxycarbonylmethyloxime *XXXII*. Compound *XVI* reacted in the presence of NaH with diethyl ethoxycarbonylmethanephosphonate to derivative *XXXIII*, having an oxirane ring in the molecule. 2,2,4,4-Tetramethyl-5-(4-propionylphenyloxy-3-methyl-2-pentenyl)-1,3-dioxolane (*XXXIV*) was prepared on reaction of epoxy compound *XVI* with anhydrous acetone in the presence of a catalytic amount of $FeCl_3$. The terminal

TABLE I

Some characteristic data of compounds of the type

$$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OC_6H_4ZC_2H_5$$

No	Z	Yield, %	Formula (mol.wt.)	Calculated/Found	
				% C	% H
I	CH(OH)	80	$C_{19}H_{28}O_2$	78·42	9·85
			(288·4)	78·72	9·81
II[a]	CH(OH)	78	$C_{19}H_{30}O_2$	78·57	10·41
			(290·4)	78·78	10·09
III	CH(O-2-THP)[b]	96	$C_{24}H_{36}O_3$	77·38	9·74
			(372·5)	77·57	9·63
IV[c]	CH(O-2-THP)	83	$C_{26}H_{42}O_4$	74·59	10·11
			(418·6)	74·50	10·36
V[c]	CH(O-2-THF)	41	$C_{25}H_{40}O_4$	74·21	9·96
			(404·6)	74·40	9·98
VI	$CH[OCO(CH_2)_{16}CH_3]$	60	$C_{37}H_{62}O_3$	80·08	11·26
			(554·9)	80·33	11·12
VII	$CH(OCOCH_2Cl)$	43	$C_{21}H_{29}ClO_3$	69·11	8·01
			(364·9)	69·37	8·37
VIII	$CH(OCOC_6H_4\text{-2-}COOCH_3)$	96[d]	$C_{28}H_{34}O_5$	74·63	7·60
			(450·5)	74·81	7·85
IX	$CH(OCOC_2H_4COOCH_3)$	96[d]	$C_{24}H_{34}O_5$	71·61	8·51
			(402·5)	71·65	8·52
X[a]	$CH(OCOC_6H_4\text{-4-}Cl)$	46	$C_{26}H_{33}ClO_3$	72·79	7·75
			(429·0)	72·91	7·71
XI	$CH(OCOCH_3)$	85	$C_{21}H_{30}O_3$	76·33	9·15
			(330·5)	76·30	9·29
XII		45	$C_{21}H_{30}O_3$	76·33	9·15
			(330·5)	76·25	9·03
XIII[e]	C=NOH	80	$C_{19}H_{27}NO_2$	75·71	9·03
			(301·3)	75·52	9·15
XIV[f]	$C{=}NOCH_2COOH$	75	$C_{21}H_{29}NO_4$	70·16	8·13
			(359·5)	69·84	8·10
XV[g]	$C{=}NOCH_2COOCH_3$	96[d]	$C_{22}H_{31}NO_4$	70·70	8·37
			(373·5)	70·82	8·12

[a] 2,3-Dihydro derivative; [b] 2-tetrahydropyranyl derivative; [c] 7-ethoxy derivative; [d] prepared on reaction of the acylation product with diazomethane; [e] calculated: 4·64% N; found: 4·44% N; ratio of the *Z*- and *E*-isomer 2 : 1, [f] calculated: 3·89% N; found: 3·73% N; [g] calculated: 3·75% N; found: 3·73% N.

TABLE II

Some characteristic data of compounds of the type

$$(CH_3)_2\underset{\diagdown O \diagup}{C-CH}(CH_2)_2C(CH_3){=}CHCH_2OC_6H_4ZC_2H_5$$

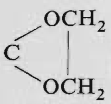
No	Z	Yield, %	Formula (mol.wt.)	Calculated/Found % C	Calculated/Found % H
XVI	CO	51	$C_{19}H_{26}O_3$ (302·4)	75·46 75·62	8·66 8·62
XVII[a]	CO	33	$C_{19}H_{26}O_4$ (318·4)	71·67 71·82	8·23 8·35
XVIII[b]	CO	50	$C_{19}H_{28}O_3$ (304·4)	74·96 74·64	9·27 8·98
XIX	CH(OH)	40	$C_{19}H_{28}O_3$ (304·4)	74·96 74·71	9·27 9·39
XX[b]	CH(OH)	49	$C_{19}H_{30}O_3$ (306·4)	74·47 74·26	9·87 9·84
XXI	$CH[OCO(CH_2)_{16}CH_3]$	35	$C_{37}H_{62}O_4$ (570·9)	77·84 77·53	10·94 10·70
XXII[a]	$CH[OCO(CH_2)_{16}CH_3]$	—[c]	$C_{37}H_{62}O_5$ (586·9)	75·72 76·05	10·65 10·65
XXIII	$CH(OCOCH_2Cl)$	36	$C_{21}H_{29}ClO_4$ (380·9)	66·21 66·52	7·67 7·97
XXIV	$CH(OCOC_6H_4$-2-$COOCH_3)$	34	$C_{28}H_{34}O_6$ (466·6)	72·07 72·00	7·34 7·23
XXV	$CH[OCO(CH_2)_2COOCH_3]$	39	$C_{24}H_{34}O_6$ (418·5)	68·87 68·82	8·18 8·31
XXVI[a]	$CH[OCO(CH_2)_2COOCH_3]$	—[c]	$C_{24}H_{34}O_7$ (434·5)	66·34 66·38	7·89 7·71
XXVII[b]	$CH(OCOC_6H_4$-4-$Cl)$	37	$C_{26}H_{33}ClO_4$ (445·0)	70·17 70·36	7·47 7·47
XXVIII	$CH(OCOCH_3)$	33	$C_{21}H_{30}O_4$ (346·5)	72·80 72·63	8·72 8·55
XXIX	CH(O-2-THP)	38	$C_{24}H_{36}O_4$ (388·5)	74·70 74·59	9·46 9·54
XXX		43	$C_{21}H_{30}O_4$ (346·5)	72·79 72·71	10·19 9·99
XXXI[d]	C=NOH	50[e]/65[f]	$C_{19}H_{27}NO_3$ (317·4)	71·88 71·71	8·57 8·23

TABLE II
(*Continued*)

No	Z	Yield, %	Formula (mol.wt.)	Calculated/Found	
				% C	% H
XXXII[g]	$C{=}NOCH_2COOC_2H_5$	57	$C_{23}H_{33}NO_5$ (403·5)	68·46 68·22	8·24 7·90
XXXIII	$C{=}CHCOOC_2H_5$	44	$C_{23}H_{32}O_4$ (372·5)	74·16 74·03	8·66 8·61
XXXIV[h]	CO	44	$C_{22}H_{32}O_4$ (360·5)	73·29 73·03	8·94 8·88
XXXV[i]	CO	38	$C_{25}H_{31}ClO_3S$ (447·0)	67·16 67·28	6·99 6·63
XXXVI[j]	CO	60	$C_{19}H_{28}O_4$ (320·4)	71·22 70·92	8·81 9·08
XXXVII[k]	$C{=}NOCH_2COOCH_3$	39	$C_{22}H_{31}NO_5$ (389·5)	67·84 67·96	8·02 7·82

[a] 2,3; 6,7-Diepoxy derivative; [b] 2,3-dihydro derivative; [c] isolated as a by-product of the preparation of monoepoxy derivative; [d] calculated: 4·41% N; found: 4·47% N; [e] yield of the epoxidation of oxime; [f] yield of the oximation of epoxide; [g] calculated: 3·47% N; found: 3·65% N; [h] 6,7-acetonyl derivative; [i] 7-hydroxy-6-(4-chlorophenylthio) derivative; [j] 6,7-dihydroxy derivative; [k] calculated: 3·60% N; found: 3·58% N.

oxirane ring of compound *XVI* was further modified with 4-chlorothiophenol, under formation of 7-hydroxy derivative *XXXV*. Another modifying reaction, involving the reactivity of the oxirane ring and affording products analogous to those formed by detoxication mechanisms in the insect organism, was the reaction of compound *XVI* with aqueous $HClO_4$ solution. 6,7-Dihydroxy derivative *XXXVI* was the reaction product.

The second large group of substances with the activity of juvenile hormone, containing an oxygen heterocycle in the molecule, were the products of ketalization of 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone and 4-(3,7-dimethyl-2-octenyloxy)propiophenone or their 7-ethoxy-, 7-propoxy-, 7-(2-chloroethoxy)-, 7-(2-cyanoethoxy)-, and 7-cyclopropylmethoxy derivatives (compounds *XXXVIII*–*LV*, Table III). Identical products *XL*–*LV* were also obtained, when the reaction sequence was reversed, *i.e.* on alkoxylation of the products of ketalization.

The oxygen-containing heterocycle in the substituent of the aromatic part of the molecule also occurred in compounds *IV* and *V*. Compound *IV* was prepared on ad-

TABLE III

Some characteristic data of compounds of the type

$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OC_6H_4CC_2H_5$

O O

Z

No	Z	Yield, %	Formula (mol.wt.)	Calculated/Found % C	Calculated/Found % H
XXXVIII	$CH_2CH(CH_2OH)$	31[a]	$C_{22}H_{32}O_4$	73·30	8·95
			(360·5)	73·60	8·81
XXXIX[b]	$CH_2CH(CH_3)$	46·5[c]	$C_{22}H_{34}O_3$	76·26	9·89
			(346·5)	76·35	10·21
		7-ethoxy derivatives			
XL	CH_2CH_2	94[d]	$C_{23}H_{36}O_4$	73·36	9·64
			(376·5)	73·49	9·65
XLI	$CH_2CH(CH_3)$	44·5[a]	$C_{24}H_{38}O_4$	73·80	9·81
			(390·5)	73·64	9·58
XLII	$CH_2CH(CH_2Cl)$	31·5[a]	$C_{24}H_{37}ClO_4$	67·82	8·78
			(425·0)	67·82	8·91
XLIII	$CH_2CH(CH_2OH)$	30[a]	$C_{24}H_{38}O_5$	70·90	9·42
			(406·5)	70·87	9·41
XLIV	$CH_2CH(CH_2OCH_3)$	30[a]	$C_{25}H_{40}O_5$	71·39	9·59
			(420·6)	71·41	9·34
XLV	$CH(C_4H_9)CH(C_4H_9)$	46·5[a]	$C_{31}H_{52}O_4$	76·18	10·73
			(488·7)	76·24	10·68
XLVI	$CH_2CH_2CH(C_7H_{15})$	37[a]	$C_{31}H_{52}O_4$	76·18	10·73
			(488·7)	75·95	10·67
XLVII	$CH_2C(CH_3)_2CH_2$	50[a]	$C_{26}H_{42}O_4$	74·60	10·11
			(418·6)	74·51	10·19
XLVIII[b]	$CH_2CH(CH_3)$	41[e]	$C_{24}H_{40}O_4$	73·43	10·27
			(392·6)	73·47	10·38
XLIX[b]	$CH_2CH(CH_2Cl)$	31[a]	$C_{24}H_{39}ClO_4$	67·50	9·21
			(427·0)	67·66	9·26
L[b]	$CH_2CH(CH_2OCH_3)$	30[a]	$C_{25}H_{42}O_5$	71·05	10·02
			(422·6)	70·83	9·69
		7-propoxy derivatives			
LI	CH_2CH_2	43[e]	$C_{24}H_{38}O_4$	73·80	9·81
			(390·5)	73·77	9·49

TABLE III
(*Continued*)

No	Z	Yield, %	Formula (mol.wt.)	Calculated/Found % C	Calculated/Found % H
LII[b]	$CH_2CH(CH_3)$	45[c]	$C_{25}H_{42}O_4$ (406·6)	73·85 73·85	10·41 10·56
	7-cyclopropylmethoxy derivative				
LIII[b]	$CH_2CH(CH_2Cl)$	47[a]	$C_{26}H_{41}ClO_4$ (452·5)	68·92 69·13	9·12 9·21
	7-(2-chloroethoxy) derivative				
LIV	CH_2CH_2	42[a]	$C_{23}H_{35}ClO_4$ (411·0)	67·21 67·09	8·58 8·73
	7-(2-cyanoethoxy) derivative				
LV	CH_2CH_2	84[d]	$C_{24}H_{35}NO_4$ (401·5)	71·79 71·98	8·79 8·60

[a] Yield of ketalization of the keto compound; [b] 2,3-dihydro derivative; [c] yield of alkylation of the ketal; [d] yield of transketalization; [e] yield of alkoxylation of the ketal.

dition of 2,3-dihydro-4*H*-pyrane to a corresponding hydroxy compound under catalysis with *p*-toluenesulfonic acid, while compound *V* was formed on reaction of the hydroxy compound with anhydrous tetrahydrofuran, in the presence of an equimolar amount of SO_2Cl_2 and triethylamine as a base.

EXPERIMENTAL

All the products from the reactions described were purified chromatographically on silica gel columns (60—120 μm, Service laboratory of this Institute). The silica gel used contained 8% (by weight) of water. Columns of alumina (Woelm) with 2% of water were also used. The homogeneity of the chromatographic fractions was checked by TLC on silica gel G (Merck) and Silufol with a luminescent indicator (Kavalier). Detection was carried out by spraying with H_2SO_4 and carbonization or in UV light of 254 nm wavelength. The ratio of the *cis*- and *trans*-isomers of compound *XVI* was determined by GLC on Chromosorb W impregnated with 5% of OV-17-1F; the ratio of *E*- and *Z*-isomers of compound *XIII* was determined by means of ^{1}H-NMR spectrometry. The chemical structure of the compounds prepared was confirmed by elemental analysis and in some cases by IR (UR-20 spectrometer, CCl_4), mass (AEI MS-902 spectrometer, 70 eV ionization potential) and ^{1}H-NMR (Varian HA-100, $CDCl_3$, TMS, 100 MHz) spectrometry.

Compounds *I*, *II*

A solution of 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone or 4-(3,7-dimethyl-2-octenyloxy)propiophenone (0·01 mol) in diethyl ether was added dropwise and under stirring and exclusion of atmospheric moisture, at 10—20°C, to a suspension of $LiAlH_4$ (5 mmol, 20 mass % excess) in diethyl ether. The mixture was refluxed for 30 min. After cooling with ice and dilution with diethyl ether the unreacted hydride was decomposed under stirring with icy water and dilute H_2SO_4. The ethereal layer was washed with a saturated NaCl solution, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography.

Compounds *III*, *IV*

A catalytic amount of *p*-toluenesulfonic acid was added to a solution of compound *I* or of its 7-ethoxy derivative[1] (0·01 mol) in 2,3-dihydro-4*H*-pyrane (0·01 mol) under stirring and at room temperature and the mixture was stirred for 10 min. After dilution with water and extraction with diethyl ether the product was isolated from the ethereal layer and worked up as above.

Compound *V*

A solution of SO_2Cl_2 (2 mmol) in 5 ml of anhydrous tetrahydrofuran was added to a solution of 7-ethoxy derivative of compound *I* (ref.[1]) (2 mmol) and triethylamine (8 mmol) in 6 ml of anhydrous tetrahydrofuran at 0°C and under stirring, and the stirring was continued for 15 min at the same temperature. The mixture was filtered, diluted with water and extracted with diethyl ether. Further procedure was the same as that used above.

Compounds *VI*—*XI*

Chloride or anhydride of respective monocarboxylic acid (0·01 mol) was added gradually at room temperature to a stirred solution of compound *I* or *II* (0·01 mol) and anhydrous pyridine (0·01 mol), with an addition of anhydrous dimethylformamide if necessary, and the mixture was allowed to stand at room temperature for 30 min if acetic anhydride was used, or overnight if acid chloride was employed. The isolation of the product was the same as in the preceding cases.

When compounds *VIII* and *IX* were prepared a mixture of compounds *I* (0·01 mol), dicarboxylic acid anhydride (0·01 mol) and anhydrous pyridine (0·01 mol) was heated at 60°C for 10 h and then allowed to stand at room temperature overnight. The product was isolated as described above.

Compounds *XII*, *XXXVIII*—*LV*

A mixture of 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone, 4-(3,7-dimethyl-2-octenyloxy)-propiophenone or its 7-ethoxy-, 7-propoxy-, 7-(2-chloroethoxy)-, 7-(2-cyanoethoxy)-, and 7-cyclopropylmethoxy derivatives (0·01 mol), a vicinal dihydroxy compound (0·01 mol, 20% mass % excess) and a catalytic amount of *p*-toluenesulfonic acid was refluxed for 1 h in an apparatus provided with a device for azeotropic distillation and benzene (or toluene) as solvent. After evaporation of the predominant part of benzene under reduced pressure the residue was extracted between diethyl ether and a saturated $NaHCO_3$ solution. The ethereal layer was dried and evaporated and the residue was worked up as in the preceding cases.

Compounds *XIII*, *XXXI*

Powdered NaOH (0·02 mol) was added under stirring and at 15—20°C to a solution of 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone or compound *XVI* (0·01 mol) in 96% ethanol and when it was dissolved completely hydroxylamine hydrochloride (0·03 mol) was added to the solution. The mixture was allowed to stand overnight and then the main part of ethanol was evaporated. The residue was partitioned between ether and a saturated $NaHCO_3$ solution. After separation, washing and drying of the ethereal phase it was evaporated and the residue chromatographed on a 100-fold amount of alumina with light petroleum containing increasing amounts of diethyl ether.

Compound *XIV*

Sodium acetate (0·04 mol) was added to a solution of 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone (0·01 mol) in 90% ethanol at 15—20°C and under stirring and when all sodium acetate had gone into solution carboxymethoxylamine semihydrochloride (0·02 mol) was added to the mixture which was then refluxed for 30 min. After cooling to room temperature the mixture was partitioned between diethyl ether and 1% K_2CO_3 solution in water. The ethereal layer was evaporated and the residue treated as above to afford the required product.

Compounds *XVI*—*XXXI*, *XXXVII*

A solution of an equimolar amount of monoperphthalic acid in anhydrous diethyl ether (in the case of diepoxy derivative as the main product a double amount of the equimolecular amount) was added dropwise under stirring and at 10—20°C to 4-(3,7-dimethyl-2,6-octadienyloxy)propiophenone, 4-(3,7-dimethyl-2-octenyloxy)propiophenone, compounds *I*—*XIII* and *XV* (0·01 mol) and the mixture was allowed to stand at 10—20°C for half-an-hour. It was then partitioned between an aqueous solution of $NaHCO_3$ and ether. The residue of the ethereal layer was worked up as described above. 1-Bromo-6,7-epoxy-3,7-dimethyl-2-octene was prepared in the same manner, but without isolation on a silica gel column, and then used for the synthesis of compound *XXX*.

Compound *XXXII*

Sodium hydride (0·01 ml) was added at 15—20°C and under stirring to a solution of compound *XXXI* (0·01 mol) in dimethylformamide. When the evolution of gas ceased ethyl bromoacetate (0·01 mol) was added to the mixture at the same temperature and the whole allowed to stand overnight. After dilution with water the mixture was extracted with ether and the extract was washed, dried and evaporated to dryness. The residue was further worked up chromatographically on alumina.

Compound *XXXIII*

NaH (0·01 mol) was added at 15—20°C to a stirred solution of diethyl ethoxycarbonylmethanephosphonate (0·01 mol) in ethylene glycol dimethyl ether and when the evolution of hydrogen ceased compound *XVI* (0·01 mol) was added dropwise and under stirring at the same temperature to the mixture, which was then refluxed for 4 h. After cooling to room temperature the mixture was diluted with water and extracted with diethyl ether. The residue of the extract was treated as above.

Compound *XXXIV*

A catalytic amount of $FeCl_3$ was added to a solution of compound *XVI* (0·01 mol) in 20 ml of anhydrous acetone and the mixture was allowed to stand at room temperature overnight. After evaporation of acetone and partition of the residue between a saturated $NaHCO_3$ solution and diethyl ether the residue of the ethereal extract was chromatographed on a column of silica gel.

Compound *XXXV*

4-Chlorothiophenol (1 mmol) was dissolved in ethanol and the solution was added at room temperature to a solution of compound *XVI* (1 mmol) in ethanol. After mixing 100 ml of a saturated $NaHCO_3$ solution were added and the mixture allowed to stand at room temperature overnight. Isolation of the product was carried out as above.

Compound *XXXVI*

A solution of compound *XVI* (10 mmol) in dioxane was additioned with 5 ml of water and 0·1 ml of 60% $HClO_4$ at room temperature and under stirring. After an additional 15 min of stirring the mixture was partitioned between an aqueous saturated $NaHCO_3$ solution and diethyl ether. The working up of the ethereal layer was carried out as described above.

Physico-Chemical Properties of Compounds *I*—*LV*

Boiling points (°C/13 Pa): *I* 157—160; *II* 165—168; *III* 180—183; *XI* 166—168; *XII* 180—182; *XIII* 171—173; *XVI* 168—170; *XVII* 174—176; *XVIII* 177—179; *XIX* 165—168; *XX* 174—176; *XXVIII* 173—175; *XXIX* 190—192; *XXX* 183—185; *XXXIII* 183—187; *XXXIV* 177—180; *XXXV* 212—213; *XXXIX* 190—193; *XL* 205—207; *XLI* 207—209; *XLVII* 210—212; *XLVIII* 215—217.

Melting points (°C): *XVI* 53—55; *XVII* 49—53; *XXXI* 55—58; *XXXVI* 67—69.

GLC spectra: *XVI* 80—90 weight % *trans*-isomer

IR spectra (% in CCl_4): *I*(7) 3 623 (ν(OH)), 3 465 (ν(OH) assoc.), 1 670(ν(C=C)), 1 613, 1 585, 1 515 (ν arom.); *II*(4) 3 623 (ν(OH)), 3 490 (ν(OH) assoc.), 1 613, 1 586, 1 516 (ν arom.); *VI*(4) 1 738 (ν(CO)), 1673 (ν(C=C)), 1 615, 1 587, 1 517 (ν arom.); *VII*(4) 1 763, 1 741 (ν(CO)), 1 672 (ν(C=C)), 1 615, 1 586, 1 517 (ν arom); *VIII*(4) 1 735 (ν(CO)), 1 674 (ν(C=C)), 1 614, 1 585, 1 517 (ν arom.); *IX*(4) 1 744, 1 732 (ν(CO)), 1 671 (ν(C=C)), 1 614, 1587, 1 517 (ν arom.); *X*(4) 1 724, 1 713 (ν(CO)), 1 652 (ν(C=C)), 1 615, 1 597, 1 522, 1 517 (ν arom.); *XIII*(5) 3 602 (ν(OH)), 1 673 (ν(C=C)), 1 606 (ν(C=N)); *XIV*(4) 3 534 (ν(OH)), 1 728, 1 717 (ν(CO)), 1 673 (ν(C=C)), 1 608 (ν(C=N)); *XV*(4) 1 768, 1 747 (ν(CO)), 1 679 (ν(C=C)), 1 610 (ν(C=N)); *XIX*(4) 3 623 (ν(OH)), 3 490 (ν(OH) assoc.), 1 675 (ν(C=C)), 1 613, 1 586, 1 516 (ν arom.), 1 240 (ν tetra-substituted epoxide); *XX*(4) 3 619 (νOH)), 3 480 (ν(OH) assoc.), 1 614, 1 586, 1 522, 1 517 (ν arom); *XXI*(4) 1 737, 1 730 (ν(CO)), 1 614, 1 587, 1 516 (ν arom.); *XXII*(4) 1 737, 1 731 (ν(CO)), 1 614, 1 589, 1 517 (ν arom.); *XXIII*(4) 1 763, 1 742 (ν(CO)), 1 672 (ν(C=C)), 1 615, 1 587, 1 517 (ν arom.); *XXIV*(4) 1 733 doublet (ν(CO)), 1 675 (ν(C=C)), 1 585, 1 613, 1 516 (ν arom.); *XXV*(4) 1 744, 1 732 (ν(CO)), 1 673 (ν(C=C)), 1 614, 1 587, 1 517 (ν arom.); *XXVII*(4) 1 724, 1 712 (ν(CO)), 1 615, 1 597, 1 522, 1 517 (ν arom.); *XXXI*(3) 3 601 (ν(OH)), 3 300 (ν(OH) assoc.), 1 675 (ν(C=C)), 1 607 (ν(C=N)); *XXXIII*(5) 1 713, 1 694 (ν(CO)), 1 623 (ν(C=C)); *XXXVI*(5) 3 599 (ν(OH)), 3 465 (ν(OH) assoc.), 1 716, 1 698, 1 685 (ν(CO)); *XXXVIII*(5) 3 605 (ν(OH)); *XLII*(3) 1 611, 1 584, 1 512 (ν arom.), 1 364, 1 381 (δ_s gem. CH_3), 1 172 (ν_{as} dioxol), 1 075, 1 056 (ν_s dioxol); *XLIII*(5) 3 605 (ν(OH)), 1 363 (δ_s gem. CH_3), 1 388 (δ_s CH_3); *XLIV*(6) 1 611, 1 585, 1 509, 1 497 (ν arom.), 1 459 (δ_{as} CH_3), 1 369 (δ_s gem. CH_3), 1 380, 1 387 (δ_s CH_3), 1 247 (ν(C—O)), 1 160 (ν_{as} dioxol), 1 048 (ν_s dioxol); *XLIX*(3) 1 604, 1 586, 1 515 (ν arom.), 1362, 1380 (δ_s gem. CH_3), 1173 (ν_{as} dioxol), 1074, 1058 (ν_s dioxol); *LIII*(4) 1611, 1585, 1514 (ν arom.), 1381 (δ_s CH_3), 1365 (δ_s gem. CH_3), 1173 (ν_{as} dioxol), 1058 (ν_s dioxol).

Mass spectra: *IV* 418 ($C_{26}H_{42}O_4$), 236 ($C_{14}H_{20}O_3$), 207 ($C_{12}H_{15}O_3$), 87 ($C_5H_{11}O$); *V* 404 ($C_{25}H_{40}O_4$), 222 ($C_{13}H_{18}O_3$), 193 ($C_{11}H_{13}O_3$), 87 ($C_5H_{11}O$); *XII* 330 ($C_{21}H_{30}O_3$), 301 ($C_{19}H_{25}O_3$), 165 ($C_9H_9O_3$), 121 ($C_7H_5O_2$), 69 (C_5H_9); *XV* 373 ($C_{22}H_{31}NO_4$); *XVI* 302 ($C_{19}H_{26}O_3$), 273 ($C_{17}H_{21}O_3$), 153 ($C_{10}H_{17}O$), 151 ($C_9H_{11}O_2$), 150 ($C_9H_{10}O_2$), 121 ($C_7H_5O_2$), 71 (C_4H_7O); *XXIII* 380/382 ($C_{21}H_{29}ClO_4$), 287 ($C_{19}H_{27}O_2$), 269/271 ($C_{14}H_{18}ClO_3$), 228/230 ($C_{11}H_{13}ClO_3$), 199/201 ($C_9H_8ClO_3$), 153 ($C_{10}H_{17}O$), 135 ($C_9H_{11}O$), 81 (C_6H_9), 71 (C_4H_7O); *XXVIII* 346 ($C_{21}H_{30}O_4$), 303 ($C_{19}H_{27}O_3$), 287 ($C_{19}H_{27}O_2$), 194 ($C_{11}H_{14}O_3$), 165 ($C_9H_9O_3$), 153 ($C_{10}H_{17}O$), 135 ($C_9H_{11}O$), 123 ($C_7H_7O_2$), 81 (C_6H_9), 71 (C_4H_7O); *XXX* 346 ($C_{21}H_{30}O_4$), 317 ($C_{19}H_{25}O_4$), 165 ($C_9H_9O_3$), 153 ($C_{10}H_{17}O$), 121 ($C_7H_5O_2$), 81 (C_6H_9), 71 (C_4H_7O); *XXXI* 317 ($C_{19}H_{27}NO_3$), 165 ($C_9H_{11}NO_2$), 153 ($C_{10}H_{17}O$), 81 (C_6H_9), 71 (C_4H_7O); *XXXIII* 372 ($C_{23}H_{32}O_4$), 327 ($C_{21}H_{27}O_3$), 220 ($C_{13}H_{16}O_3$), 174 ($C_{11}H_{10}O_2$), 153 ($C_{10}H_{17}O$), 81 (C_6H_9), 71 (C_4H_7O); *XXXIV* 360 ($C_{22}H_{32}O_4$), 345 ($C_{21}H_{29}O_4$), 211 ($C_{13}H_{23}O_2$), 199 ($C_{12}H_{23}O_2$), 197 ($C_{12}H_{21}O_2$), 153 ($C_{10}H_{17}O$), 151 ($C_9H_{11}O_2$), 135 ($C_{10}H_{15}$), 129 ($C_7H_{13}O_2$), 121 ($C_7H_5O_2$), 81 (C_6H_9); *XXXV* 446/448 ($C_{25}H_{31}ClO_3S$), 388/390 ($C_{22}H_{25}ClO_2S$), 297/299 ($C_{16}H_{22}ClOS$), 150 ($C_9H_{10}O_2$), 121 ($C_7H_5O_2$), 81 (C_6H_9), 59 (C_3H_7O); *XL* 376 ($C_{23}H_{36}O_4$), 361 ($C_{22}H_{33}O_4$), 347 ($C_{21}H_{31}O_4$), 165 ($C_9H_9O_3$), 101 ($C_5H_9O_2$), 87 ($C_5H_{11}O$); *XLII* 424/426 ($C_{24}H_{37}ClO_4$), 395/397 ($C_{22}H_{32}ClO_4$), 349/351 ($C_{20}H_{26}ClO_3$), 213/215 ($C_{10}H_{10}ClO_3$), 183 ($C_{12}H_{23}O$), 149/151 ($C_6H_{10}ClO_2$), 137 ($C_{10}H_{17}$); *XLV* 442 ($C_{29}H_{46}O_3$), 413 ($C_{27}H_{41}O_3$), 277 ($C_{17}H_{25}O_3$), 87 ($C_5H_{11}O$); *XLVI* 488 ($C_{31}H_{52}O_4$), 473 ($C_{30}H_{49}O_4$), 459 ($C_{29}H_{47}O_4$), 277 ($C_{17}H_{25}O_3$), 87 ($C_5H_{11}O$): *XLVII* 418 ($C_{26}H_{42}O_4$), 403 ($C_{25}H_{39}O_4$), 389 ($C_{24}H_{37}O_4$), 207 ($C_{12}H_{15}O_3$), 143 ($C_8H_{15}O_2$), 87 ($C_5H_{11}O$); *XLIX* 426/428 ($C_{24}H_{39}ClO_4$), 411/413 ($C_{23}H_{36}ClO_4$), 397/399 ($C_{22}H_{34}ClO_4$), 351/353 ($C_{20}H_{28}ClO_3$), 213/215 ($C_{10}H_{10}ClO_3$), 149/151 ($C_6H_{10}ClO_2$), 120/122 ($C_4H_5ClO_2$), 87 ($C_5H_{11}O$); *LIII* 452/454 ($C_{26}H_{41}ClO_4$), 437/439 ($C_{25}H_{38}ClO_4$), 423/425 ($C_{24}H_{36}ClO_4$), 397/399 ($C_{22}H_{34}ClO_4$), 380/382 ($C_{22}H_{33}ClO_3$), 351/353 ($C_{20}H_{28}ClO_3$), 331 ($C_{21}H_{31}O_3$), 213/215 ($C_{10}H_{10}ClO_3$); *LV* 372 ($C_{22}H_{30}NO_4$), 208 ($C_{13}H_{22}NO$), 165 ($C_9H_9O_3$).

^{1}H-NMR spectra (δ): *XIII* 1·18 (t, 3 H, $J = 7$) and 1, 21 (t, 3 H, $J = 7$), 1·61 (s, 3 H), 1·68 (s, 3 H), 1·74 (s, 3 H), 1·95—2·2 (m, 4 H), 2·80 (q, 2 H, $J = 7$) and 3·48 (q, 2 H, $J = 7$), 4·56 (d, 2 H, $J = 6·5$), 5·09 (m, H), 5·48 (m, H), 6·90 (d, 2 H, $J = 8·5$), 7·55 (d, 2 H, $J = 8·5$); *XIV* 1·18 (t, 3 H, $J = 7$), 1·61 (s, 3 H), 1·68 (s, 3 H), 1·74 (s, 3 H), 1·95—2·2 (m, 4 H), 2·80 (q, 2 H, $J = 7$), 4·56 (d, 2 H, $J = 7$), 4·74 (s, 2 H), 5·09 (m, H), 5·48 (m, H), 6·88 (d, 2 H, $J = 8·5$), 7·55 (d, 2 H, $J = 8·5$); *XV* 1·18 (t, 3 H, $J = 7$), 1·61 (s, 3 H), 1·68 (s, 3 H), 1·74 (s, 3 H), 1·85—2·2 (m, 4 H), 2·80 (q, 2 H, $J = 7$), 3·75 (s, 3 H), 4·55 (d, 2 H, $J = 6·5$), 4·71 (s, 2 H), 5·10 (m, H), 5·48 (m, H), 6·87 (d, 2 H, $J = 8·5$), 7·54 (d, 2 H, $J = 8·5$); *XVI* 1·18 (t, 3 H, $J = 7$), 1·25 (s, 3 H), 1·28 (s, 3 H), 1·50—1·8 (m, 2 H), 1·76 (s, 3 H), 2·69 (t, H, $J = 5·5$), 2·22 (m, 2 H), 2·90 (q, 2 H, $J = 7$), 4·58 (d, 2 H, $J = 6·5$), 5·52 (m, H, $J = 6·5$), 6·90 (d, 2 H, $J = 8·5$), 7·90 (d, 2 H, $J = 8·5$); *XVII* 1·28 (s, 3 H), 1·30 (s, 3 H), 1·47 (s, 3 H), 1·50—1·8 (m, 4 H), 1·91 (t, 3 H, $J = 7$), 2·71 (m, H), 2·92 (q, 2 H, $J = 7$), 3·06 (m, H), 4·08 (m, H), 4·31 (q, H), 6·96 (d, 2 H, $J = 8·5$), 7·91 (d, 2 H, $J = 8·5$); *XXX* 1·23 (s, 6 H), 1·33 (t, 3 H, $J = 7·5$), 1·54 (m, 2 H), 1·75 (s, 3 H), 1·79 (q, 2 H, $J = 7·5$), 2·19 (t, 2 H), 3·50 (m, H), 3·60—4·0 (m, 4 H), 4·46 (d, 2 H, $J = 6·5$), 5·48 (t, H), 6·72 (d, 2 H, $J = 8·5$), 7·23 (d, 2 H, $J = 8·5$); *XXXIII* 1·09 (t, 3 H, $J = 7$), 1·27 (s, 3 H), 1·30 (t, 3 H, $J = 7$), 1·31 (s, 3 H), 1·76 (s, 3 H), 1·50—1·8 (m, 2 H), 2·23 (m, 2 H), 2·71 (t, H, $J = 6$), 3·08 (q, 2 H, $J = 7$), 4·19 (q, 2 H, $J = 7$), 4·55 (d, 2 H, $J = 7$), 5·54 (m, H), 5·98 (s, H), 6·88 (d, 2 H, $J = 8·5$), 7·40 (d, 2 H, $J = 8·5$); *XXXV* 1·21 (t, 3 H), 1·24 (s, 3 H), 1·32 (s, 3 H), 1·72 (s, 3 H), 1·50—2·0 (m, 2 H), 2·1—2·5 (m, 2 H), 2·94 (q, 2 H, $J = 7$), 3·0 (m, H), 4·52 (d, 2 H, $J = 6·5$), 5·34 (m, H), 6·89 (d, 2 H, $J = 8·5$), 7·92 (d, 2 H, $J = 8·5$), 7·18 (d, 2 H, $J = 8·5$), 7·38 (d, 2 H, $J = 8·5$); *XXXVI* 1·17 (s, 3 H), 1·21 (s, 3 H), 1·21 (t, 3 H, $J = 7$), 1·76 (s, 3 H), 1·30—1·8 (m, 2 H), 2·0—2·4 (m, 2 H), 2·93 (q, 2 H), 3·35 (dd, H, J = 3·0, J = 9·0), 4·60 (d, 2 H, J = 6), 5·53 (t, H), 6·92 (d, 2 H, J = 8·5), 7·93 (d, 2 H, J = 8·5).

The elemental analyses were carried out by Mrs A. Froňková, Mrs E. Sýkorová, Mrs J. Konečná and Mrs Y. Černá (head of the laboratory Dr J. Horáček); Gas–liquid chromatography analyses were carried out by Mr J. Krahulec (head of the laboratory Dr M. Ryba). The mass spectra were measured and interpreted by Dr K. Ubik and Dr J. Kohoutová (head of the laboratory Dr L. Dolejš); the IR *spectra were measured by Mrs K. Matoušková, Mr P. Formánek and interpreted by Dr P. Fiedler (head of the laboratory Dr J. Smolíková); the* ^{1}H-NMR *spectra were measured and interpreted by Dr M. Synáčková (head of the laboratory Dr Z. Samek). The biological tests were made by Dr K. Sláma, Entomological Institute, Czechoslovak Academy of Sciences, Prague.*

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Translated by Ž. Procházka.