SYNTHESIS AND REACTIONS OF SUBSTITUTED FURO[3,2-*b*]PYRROLE DERIVATIVES*

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Preparation of ethyl 2-methylfuro[3,2-*b*]pyrrole-5-carboxylate and 2-bromofuro[3,2-*b*]pyrrole-5-carboxylate, as well as alkylation and hydrolysis of ethyl 2-methylfuro[3,2-*b*]pyrrole-5-carboxylate, ethyl furo[3,2-*b*]pyrrole-5-carboxylate and ethyl (3,4-dichlorophenyl)furo[3,2-*b*]pyrrole-5-carboxylate, is described. IR, UV, ^{1}H-NMR, ^{13}C-NMR and mass spectra of the synthesized compounds were measured and interpreted.

Our previous papers[1-3] studied the condensation of ethyl azido acetate with 5-aryl-2-furaldehydes, cyclization of the obtained substituted vinyl azides to ethyl 2-arylfuro[3,2-*b*]pyrrole-5-carboxylates, and some of their reactions. In this communication we extended the study to the parent 2-furaldehyde, 5-methyl-2-furaldehyde, 5-bromo-2-furaldehyde and 5-(3,4-dichlorophenyl)-2-furaldehyde which by reaction with ethyl azido acetate gave the substituted vinyl azides *I*–*IV*. Thermolysis of compounds *I*–*IV* afforded substituted ethyl furo[3,2-*b*]pyrrole-5-carboxylates *V*, *VI*, *XII*, *XIII* and *XVIII* which were then transformed into further derivatives (Table I).

We have found that for R^1 = H or CH_3 the optimum ratio of ethyl azido acetate to the aldehyde is 4 : 1, whereas for R = 3,4-dichlorophenyl or Br optimum yields were achieved only with an eight-fold excess of azido acetate. The optimum temperature was −5 to 0°C for R = H, CH_3 or 3,4-$Cl_2C_6H_3$ and 8–10°C for R = Br. Ammonium chloride solution was added at −10°C, but in the case of the bromo derivative it was necessary to work at −40°C because at higher temperatures the reaction gave lower yields of *III*. The prepared vinyl azides *I*–*IV* are sensitive toward light and heat. They were thermolyzed in boiling xylene to give good yields of 2-substituted ethyl furo[3,2-*b*]pyrrole-5-carboxylates. Hydrolysis of the esters with sodium hydroxide afforded stable sodium salts of the acids; their structure was proved by ^{1}H-NMR spectra.

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TABLE I

Substituted 2-azido-3-(2-furyl)acrylates (*II*, *III*) and substituted furo[3,2-b]pyrroles (*VI*—*XXII*)

Compound	Formula (mol.wt.)	Calculated/Found				M.p., °C (yield, %)
		% C	% H	% N	% Hal	
II	$C_{10}H_{11}N_3O_3$	54·30	5·00	18·99	—	30
	(221·2)	54·32	4·88	18·83		(77)
III	$C_9H_8BrN_3O_3$	37·79	2·81	14·68	27·92	28
	(286·1)	37·82	2·76	14·48	27·86	(64)
VI[a]	$C_{11}H_{13}NO_3$	63·37	6·32	6·76	—	87
	(207·2)	63·26	6·40	6·77		(—)
VII	$C_7H_5NO_3$	55·59	3·33	9·26	—	187
	(151·1)	55·42	3·28	9·39		(67)
VIII	$C_9H_9NO_3$	60·32	5·06	8·81	—	140
	(179·2)	60·34	5·08	7·86		(86)
IX	$C_{12}H_{12}N_2O_3$	62·07	5·17	12·06	—	173
	(232·2)	62·04	5·14	12·18		(92)
X	$C_9H_7NO_5$	51·67	3·37	6·69	—	179
	(209·2)	51·62	3·40	6·61		(36)
XI	$C_{10}H_9NO_5$	53·81	4·06	6·27	—	178
	(223·2)	53·68	3·92	6·16		(62)
XII	$C_{10}H_{11}NO_3$	62·17	5·74	7·24	—	111
	(193·2)	62·15	5·72	7·22		(97)
XIII[a]	$C_{12}H_{15}NO_3$	65·13	6·83	6·32	—	78
	(221·3)	65·32	6·91	6·36		(—)
XIV	$C_8H_7NO_3$	48·84	4·27	8·48	—	168
	(165·1)	48·72	4·20	8·39		(52)
XV	$C_{10}H_{11}NO_3$	62·17	5·74	7·24	—	140
	(193·2)	62·30	5·58	7·32		(68)
XVI	$C_{13}H_{14}N_2O_3$	63·39	5·73	11·37	—	119
	(246·3)	63·28	5·72	11·61		(92)
XVII	$C_9H_8BrNO_3$	41·88	3·12	5·42	30·96	120
	(258·1)	41·80	3·08	6·06	31·24	(96)
XIX	$C_{17}H_{15}Cl_2NO_3$	57·97	4·29	3·39	20·13	97
	(352·2)	57·90	4·30	3·89	20·18	(85)
XX	$C_{13}H_7Cl_2NO_3$	38·49	2·38	4·73	23·95	156
	(296·1)	38·36	2·42	4·58	23·37	(56)
XXI	$C_{15}H_{11}Cl_2NO_3$	55·57	3·42	4·32	21·87	194
	(324·2)	55·50	3·40	4·26	21·92	(73)
XXII	$C_{18}H_{14}Cl_2N_2O_3$	57·31	3·74	7·43	18·80	142
	(377·2)	57·30	3·72	7·51	18·72	(86)

[a] B.p.: *VI* 114°C/0·66 kPa; *XIII* 128°C/0·4 kPa.

The nitrogen atom in the substituted furo[3,2-*b*]pyrrole system was alkylated using phase-transfer catalysis[4,5] and the obtained ethyl derivatives were saponified with sodium hydroxide to give the corresponding acids. Acids with non-alkylated nitrogen atom of the furo[3,2-*b*]pyrrole system were obtained in lower yields and decomposed in solution whereas alkylated acids were more stable. Reaction of ethyl furo[3,2-*b*]pyrrole-5-carboxylates with acrylonitrile in pyridine in the presence of benzyltrimethylammonium hydroxide (Triton B) gave the corresponding cyanoethyl derivatives *IX*, *XVI* and *XVII*. The compound *IX* was hydrolyzed to the dicarboxylic acid *XI*. Under conditions of phase-transfer catalysis, the reaction of ethyl chloro acetate with *I* was accompanied by hydrolysis and led to the dicarboxylic acid *X*.

IR spectral data of the prepared compounds agree well with the published[1-3] values (Table II). UV spectra of compounds *V*–*XVII* exhibit maxima in the region 290 to

TABLE II

Infrared (ν, cm^{-1}) and ultraviolet (λ_{max}, nm) spectra of compounds *II*–*XXII*

Compound	ν(C=O)	ν(C=C)	ν(NH)	λ_{max}	log ε
II[a]	1 710	1 610	—	345	4·58
III[a]	1 700	1 580	—	348	4·53
VI	1 675	1 540	—	296	4·50
VII	1 680	1 550	3 415	292	4·45
VIII	1 660	1 545	—	293	4·47
IX	1 685	1 540	—	302	4·56
X[b]	1 650	1 560	—	298	4·49
XI[b]	1 655	1 560	—	298	4·46
XII	1 690	1 580	3 450	307	4·53
XIII	1 670	1 545	—	309	4·52
XIV	1 645	1 565	3 465	302	4·50
XV	1 660	1 550	—	302	4·50
XVI	1 685	1 580	—	306	4·53
XVII	1 695	1 530	3 390	304	4·51
XVIII[c]	1 665	1 540	3 450	343	4·72
XIX[c]	1 680	1 545	—	346	4·76
XX[c]	1 630	1 580	3 460	347	4·70
XXI[c]	1 670	1 530	—	348	4·71
XXII[c]	1 685	1 570	—	343	4·78

[a] Compounds *II* and *III* exhibit marked $\nu(N_3)$ at 2 200 cm^{-1} and 2 150 cm^{-1}; [b] ν(C=O) for the group at $C_{(5)}$; [c] compounds *XVIII*–*XXII* display a second λ_{max} (log ε): *XVIII* 364 (4·70), *XX* 362 (4·69), *XIX* 362 (4·72), *XXI* 363 (4·70), *XXII* 358 (4·72).

310 nm, compounds *XVIII*–*XXII* display two absorption bands at about 345 to 360 nm. There was no marked effect of substituent bonded to the nitrogen atom.

^{1}H-NMR spectra of compounds *II* and *III* (Table III) exhibited a long-range coupling through five bonds between the H_b proton of the furan nucleus and the H_d olefinic proton. Judging from the coupling constant $J_{b,d}$ (0·6 Hz), it can be assumed that in the studied compounds the form with *s-cis* relation of the furan ring and the double bond predominates. This conformation allows an enhanced coupling of the *W* type. This stereospecific interaction was already utilized in determination of the predominant *s-cis* conformation in ethylenic derivatives of five-membered heterocycles[6–9]. The compounds *II* and *III* are substituted vinyl azides which are cyclized with elimination of nitrogen to give substituted furo[3,2-*b*]pyrroles. Thermolysis

TABLE III

^{1}H-NMR chemical shifts (δ, ppm) of substituted ethyl 2-azido-3-(2-furyl)acrylates (*II*, *III*) and furo[3,2-*b*]pyrroles (*V*–*XXII*)

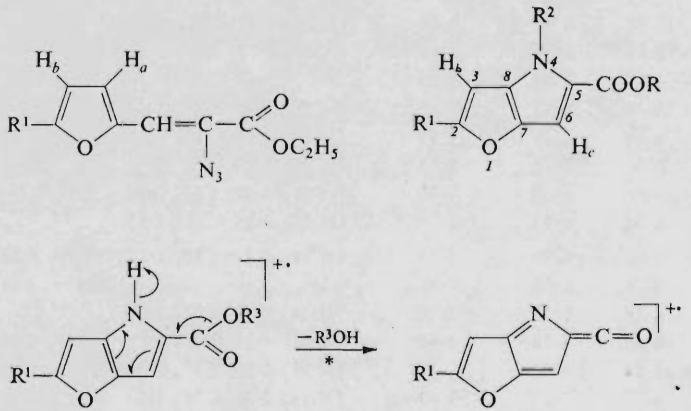
Compound	H_b[a]	H_c[b]	R_1[c]	Other signals
II	6·11	—	2·44	H_a 6·99; H_d 6·93; OCH_2 4·33; CH_3 1·36
III	6·43	—	—	H_a 7·03; H_d 6·75; OCH_2 3·83; CH_3 1·37
V	6·38	6·79	7·44	OCH_2 4·32; CH_3 1·29
VI	6·38	6·79	7·44	OCH_2 4·23; CH_3 1·29; NCH_2 4·46; CH_3 1·39
VII	6·49	6·61	6·64	
VIII	6·45	6·95	7·52	NCH_2 4·45; CH_3 1·41
IX	6·54	6·85	7·51	OCH_2 4·31; CH_3 1·36; NCH_2 4·64; CH_2 2·84
X	6·68	6·72	7·65	NCH_2 2·49
XI	6·65	6·67	7·70	NCH_2 4·44; CH_2 2·54
XII	6·04	6·72	2·35	OCH_2 4·25; CH_3 1·33
XIII	6·00	6·70	2·35	OCH_2 4·22; CH_3 1·27; NCH_2 4·83; CH_2 1·38
XIV	6·28	6·66	2·40	
XV	6·28	6·47	2·28	NCH_2 4·31; CH_3 1·10
XVI	6·45	6·74	2·40	OCH_2 4·18; CH_3 1·25; NCH_2 4·59; CH_2 2·96
XVII	6·44	6·75	—	OCH_2 4·35; CH_3 1·36
XVIII	6·77	7·32	7·59–8·05	OCH_2 4·36; CH_3 1·37
XIX	6·66	7·31	7·54–7·83	OCH_2 4·09; CH_3 1·16; NCH_2 5·05; CH_3 1·28
XX	6·61	7·20	7·59–7·91	
XXI	6·64	7·39	7·58–7·88	NCH_2 4·21; CH_3 1·24
XXII	6·80	7·10	7·25–7·75	OCH_2 4·30; CH_3 1·35; NHC_2 4·63; CH_2 2·91

[a] Compounds *II*, *III*: $J_{a,b}$ = 3·2 Hz, $J_{b,d}$ = 0·6 Hz; [b] compounds *V*–*XI*: $J_{b,c}$ = 0·8 Hz, *XII* to *XVI*: $J_{b,c}$ = 0·9 Hz, *XVIII*–*XXII*: $J_{b,c}$ = 1·0 Hz; [c] protons of the substituent R^1, compounds *XVIII*–*XII*: multiplet of the aromatic protons, compounds *V*–*XI*: $J_{2,b}$ = 2·2 Hz.

of ethyl 2-azidocinnamates to the corresponding indole derivatives was found[10] to proceed *via* substituted azirines and it was therefore of interest to know whether also in our case a substituted azirine is formed. We investigated the thermolysis of the relatively stable ethyl 2-azido-3-(5-methyl-2-furyl)acrylate (*II*) in boiling hexadeuteriobenzene and in n-heptane at 90°C, using ^{1}H-NMR spectroscopy. In neither solvent we detected any signal in the 3 ppm region expected for the azirine.

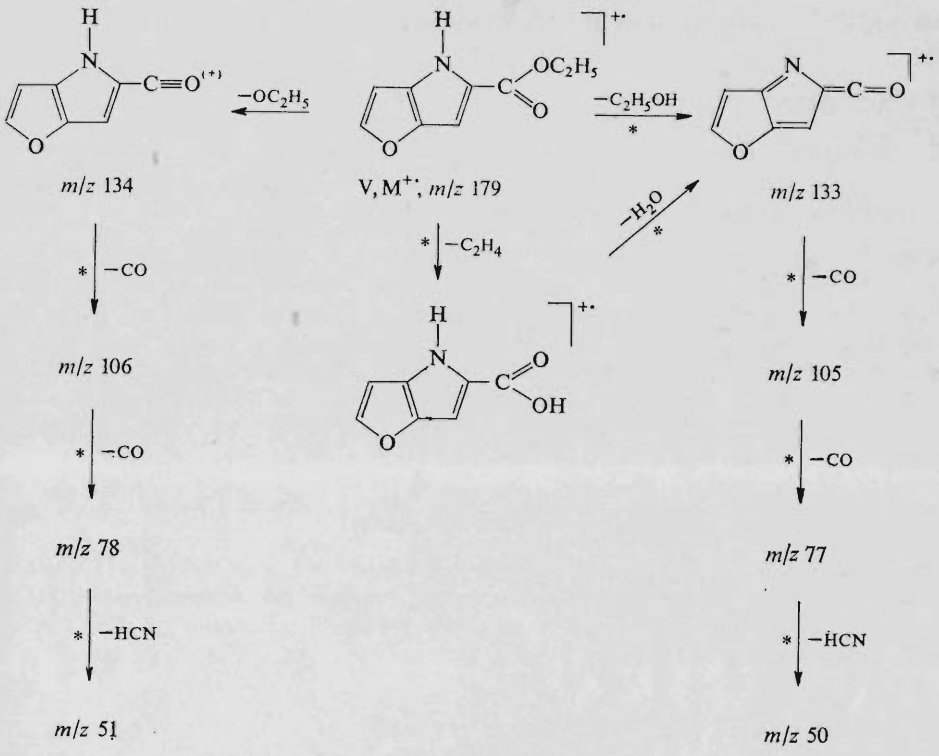
Table IV contains ^{13}C-NMR spectra of compounds *V*, *VI*, *XII* and *XIII*. The ^{13}C chemical shifts were determined from proton noise decoupled spectra. The quaternary carbon atoms were identified as lower intensity signals and in undecoupled spectrum on the basis of absence of a direct coupling with proton. Other carbon atoms were assigned by comparison of chemical shifts and coupling constants J(C—H) with the reported[11,12] data. Ethyl group at the nitrogen atom caused a downfield shift of the $C_{(5)}$ and $C_{(7)}$ signals and an upfield shift of the $C_{(6)}$ and $C_{(8)}$ signals, not affecting the $C_{(2)}$ and $C_{(3)}$ signals.

Mass spectra of compounds *V*, *VII–IX*, *XII* and *XVII* are given in the Experimental. Only peaks of relative intensity $\geq 4\%$ are listed. In the spectra of compounds *VII–IX*, the molecular ion peaks are the most abundant, in spectra of *V*, *XII* and *XVII* their intensity is greater than 50%. Main fragmentation of the molecular ions consists in the elimination of a neutral molecule R^3OH in the form of H_2O or C_2H_5OH (Scheme 1). This cleavage is analogous to that of the acids and carboxylates of the pyrrole series[13].



SCHEME 1

The fragment ion *a* (*m/z* 133) is formed also from compounds with a substituent at the pyrrole nitrogen atom (*VIII*, *IX*), it is, however, of substantially lower relative intensity. Further splitting of the ion *a*, as well as further possible splittings of the molecular ions, are given in the fragmentation scheme for the compound *V* (Scheme 2).



SCHEME 2

TABLE IV

^{13}C-NMR chemical shifts (δ, ppm) of compounds *V*, *VI*, *XXII*, *XIII*

Compound	$C_{(2)}$	$C_{(3)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	CO	CH_2	CH_3
V	148·6	98·9	125·1	96·8	128·9	147·9	162·4	60·5	14·5
VI	148·3	98·2	123·2	98·2	132·4	145·9	161·8	59·8 42·5	14·5 16·0
XII	159·4	95·3	122·2	96·6	130·4	146·8	162·5	60·3	14·5 14·9
XIII	158·7	94·3	120·9	97·8	133·4	144·5	161·7	59·2 42·1	14·6 15·7 14·2

Pesticidal activity of selected compounds *XVII* and *XIX*, determined by the published methods[14,15], was only weak and the compounds were not tested further.

EXPERIMENTAL

Compounds *I*, *IV*, *V* and *XVIII* were prepared according to ref.[1,8].

Ethyl 2-Azido-3-(5-methyl-2-furyl)acrylate (*II*)

A solution of 5-methyl-2-furaldehyde (1·1 g; 10 mmol) and ethyl azido acetate (5·16 g; 40 mmol) in ethanol (60 ml) was added at 0°C during 30 min to a solution of sodium ethoxide (prepared from 1·84 g, 0·08 gat of sodium and 60 ml of ethanol). The mixture was stirred for 60 min at 15°C, cooled to −10°C, treated with a solution of ammonium chloride (2·1 g; 40 mmol) in water (25 ml) and poured into ice-cold water. The separated product was filtered and crystallized from ether. An analogous procedure was employed for the preparation of ethyl 2-azido-3-(5-bromo-2-furyl)-acrylate (*III*), using 10·32 g (80 mmol) of ethyl azido acetate; the temperature of the mixture during the stirring was kept at 10°C and ammonium chloride was added at −40°C.

Ethyl 2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (*XII*)

A stirred solution of ethyl 2-azido-3-(5-methyl-2-furyl)acrylate (1 g) in xylene (100 ml) was refluxed for 20 min, the solvent was evaporated *in vacuo* and the obtained product *XII* was crystallized from benzene. Similar. procedure was used for the preparation of ethyl 2-bromo-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (*XVII*).

4*H*-Furo[3,2-*b*]pyrrole-5-carboxylic Acid (*VII*)

Ethyl 4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (1·79 g; 10 mmol) was dissolved in ethanol (50 ml) and a 4% solution of sodium hydroxide (20 ml) was added. The mixture was refluxed for 3 h, cooled, acidified with hydrochloric acid (1 : 1) and extracted with ethyl acetate. The organic layer was dried, taken down and the crude product *VII* crystallized from ethanol. Similarly were prepared 2-methyl-4H-furo[3,2-*b*]pyrrole-5-carboxylic acid (*XIV*) and 2-(3,4-dichlorophenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid (*XX*).

Ethyl 4-Ethylfuro[3,2-*b*]pyrrole-5-carboxylate (*VI*)

A 50% sodium hydroxide solution (30 ml), ethyl iodide (1·65 g; 11 mmol) and triethybenzylammonium chloride (0·4 g) were added to a stirred solution of *I* (1·79 g; 10 mmol) in benzene (100 ml). The resulting solution was stirred at 65°C for 4 h, cooled and shaken with water. The organic layer was separated and the aqueous one was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous sodium sulfate, taken down and the product was crystallized from methanol. Similarly were prepared ethyl 2-methyl-4-ethylfuro[3,2-*b*]-pyrrole-5-carboxylate (*XIII*) and ethyl 2-(3,4-dichlorophenyl)-4-ethylfuro[3,2-*b*]pyrrole-5-carboxylate (*XIX*).

4-Ethylfuro[3,2-*b*]pyrrole-5-carboxylic Acid (*VIII*)

A 5% solution of sodium hydroxide (20 ml) was added to a solution of *VIII* (2·07 g; 10 mmol) and the mixture was heated on a water bath for 2 h. After concentration to half of the original

volume the precipitate was filtered, dissolved in dilute ethanol, acidified with hydrochloric acid (1 : 1) and poured on ice. The precipitated product was filtered and crystallized from ethanol. Similar procedure was applied to preparation of 2-methyl-4-ethylfuro[3,2-*b*]pyrrole-5-carboxylic acid (*XV*) and 2-(3,4-dichlorophenyl)-4-ethylfuro[3,2-*b*]pyrrole-5-carboxylic acid (*XVIII*).

Ethyl 4-(2-Cyanoethyl)furo[3,2-*b*]pyrrole-5-carboxylate (*IX*)

A solution of *I* (1·79 g; 10 mmol) in pyridine was mixed with acrylonitrile (3·75 g; 7·5 mmol) and 40% ethanolic solution (0·15 ml) of trimethylbenzylammonium hydroxide. The mixture was refluxed for 20 min, cooled, taken down *in vacuo* and the product was crystallized from benzene. Similarly were prepared: ethyl 2-methyl-4-(2-cyanoethyl)-furo[3,2-*b*]pyrrole-5-carboxylate (*XVI*) and ethyl 2-(3,4-dichlorophenyl)-4-(2-cyanoethyl)furo[3,2-*b*]pyrrole-5-carboxylate (*XXII*).

4-(2-Carboxyethyl)furo[3,2-*b*]pyrrole-5-carboxylic Acid (*XI*)

A solution of *IX* (1·79 g; 10 mmol) in ethanol was refluxed with a solution of sodium hydroxide (2·12 g) in water (10 ml) until the evolution of ammonia ceased. Ethanol was removed *in vacuo*, the residue dissolved in ethanol, the solution acidified with hydrochloric acid (1 : 1) and poured on ice. The precipitate was filtered, washed with water and crystallized from ethanol.

4-Carboxymethylfuro[3,2-*b*]pyrrole-5-carboxylic Acid (*X*)

A solution of *I* (1·79 g; 10 mmol) in benzene (60 ml) was mixed with a 50% sodium hydroxide solution (30 ml), ethyl chloroacetate (1·34 g; 11 mmol) and triethylbenzylammonium bromide (0·4 g). The mixture was kept at 65°C for 4 h, cooled, treated with water (100 ml) and acidified with hydrochloric acid. The benzene layer was separated and the aqueous one extracted with benzene. The combined benzene extracts were dried over sodium sulfate, taken down and the residue was crystallized from ethanol.

Spectral Measurements

The IR absorption spectra (Table II) were taken on a UR-20 (Zeiss, Jena) spectrophotometer. Compounds *VII*, *VIII*, *X*, *XI*, *XX*, *XIV*, *XV* were measured using the KBr technique (1 mg/g KBr). Electronic absorption spectra (Table II) were recorded in methanol on a SPECORD UV VIS spectrometer (Zeiss, Jena) at room temperature; concentration $2 . 10^{-5}$—$5 . 10^{-5}$ mol . $. 1^{-1}$. ^{1}H-NMR spectra were measured on an 80 MHz Tesla BS 487C instrument. Compounds *VII*, *VIII*, *X*, *XI*, *XIV*, *XV* and *XX* were measured in hexadeuteriodimethylsulfoxide with hexamethyldisiloxane as internal standard, other compounds in deuteriochloroform (internal standard tetramethylsilane). ^{13}C-NMR spectra (Table IV) were taken on a JEOL FX-100 spectrometer (99·6 MHz) in deuteriochloroform.

Mass spectra of selected compounds were measured on an MS 902 S (AEI Manchester) mass spectrometer (direct inlet, 70 eV, trap current 100 μA, ionisation chamber temperature 80°C). Ten most abundant peaks are given with their relative intensities in parentheses: *V* 179 M^+ (77), 134 (29), 133 (100), 106 (10), 105 (16), 78 (12), 77 (24), 53 (11), 51 (14), 50 (11). *VII* 151 M^+ (100), 134 (14), 133 (81), 105 (32), 78 (19), 77 (60), 53 (26), 52 (21), 51 (20), 50 (19). *VIII* (180 (12·5), 179 M^+ (100), 164 (24), 134 (14), 133 (39), 118 (11), 77 (18), 53 (13), 52 (12), 51 (11). *IX* 233 (16), 232 M^+ (100), 204 (19), 187 (22), 164 (50), 160 (15), 133 (17), 92 (14), 53 (14), 52 (15.) *XII* 194 (11), 193 M^+ (80), 148 (27), 147 (100), 120 (9), 119 (26), 91 (9), 53 (11), 43 (51), 39 (11). *XVII* 259 (53), 257 M^+ (54), 214 (29), 213 (99), 212 (29), 211 (100), 104 (30), 76 (30), 53 (23), 50 (25).

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