REACTIONS AND SPECTRAL PROPERTIES OF ETHYL 5-AMINOFUROATE AND ITS DERIVATIVES

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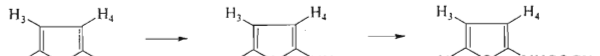
Ethyl 5-aminofuroate (*II*), prepared by reduction of ethyl 5-nitrofuroate (*I*), served for preparation of bifunctional α,β-substituted aminofurans *IV*–*IX*, acyl derivatives *IIIa*, *IIIb* and condensation product *X*. The latter reacted with diazomethane directly to afford the corresponding aziridine derivative *XI*. The synthesized compounds were characterized by spectral data (IR, UV, ^{1}H-NMR, ^{13}C-NMR (*XI*) and mass spectra).

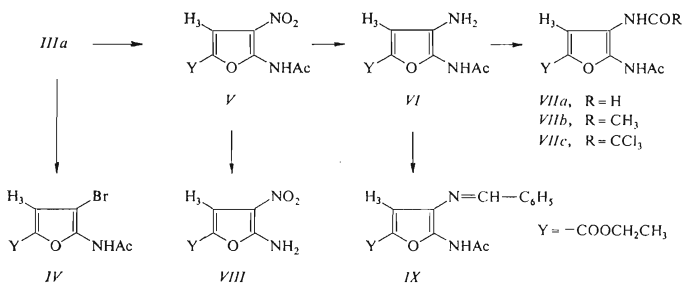
The α,β-bifunctional aminofuran derivatives are potential synthons for preparation of nitrogen containing heterocycles. Ethyl 5-aminofuroate (*II*), which can be synthesized by reduction of ethyl 5-nitrofuroate (*I*) with aluminium amalgam in water-saturated ether[1], was chosen for starting material, since it contains a stabilizing deactivation group. Even more stable are acylated aminofurans *IIIa*, *IIIb*, Scheme 1. Subsequent nitration or bromination of *IIIa* leads to ethyl 4-nitro-5-acetylamidofuroate (*V*) or ethyl 4-bromo-5-acetylamidofuroate (*VI*). A several-days bromination of *I*



I *II* *IIIa*, X = H
Y = −COOCH$_2$CH$_3$ *IIIb*, X = F

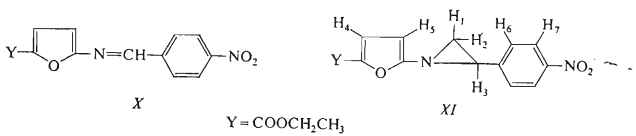
SCHEME 1

failed in contrast to a very easy bromination of *IIIa*. An attempted preparation of the corresponding azidofuran with NaN_3 in dimethyl sulfoxide and CuO as a catalyst at 100°C from *IV* resulted in a debromination under formation of *IIIa*, ref.[2]. Ethyl 4-amino-5-acetylamidofuroate (*VI*), ref.[3], prepared by reduction of *V* easily undergoes condensation with benzaldehyde to afford the imine *IX*. Aminofuran derivatives *VIIa* to *VIIc* were obtained when verifying cyclization methods[2]. Acid hydrolysis of *V* furnished ethyl 4-nitro-5-aminofuroate (*VIII*), ref.[4], Scheme 2.



SCHEME 2

Similarly as *VI*, *II* also condenses easily with 4-nitrobenzaldehyde to give the azomethine *X*, and, in contrast to other analogous azomethine derivatives[2], *X* reacts with diazomethane by a 1,3-dipolar cyclization reaction under liberation of nitrogen to form directly the aziridine derivative *XI*, Scheme 3.



The unsubstituted and substituted amino groups in aminofurans are well characterized by their reactivities and spectral properties. Basing upon chemical shifts (δ, ppm) of the ^{1}H-NMR spectrum, the electronic situation is mostly influenced by direct substitution on the amino group.

The proton signal of the —NH_2 group of *II* is seen as a singlet at 5·70, what accords with the chemical shift of that in 2-cyano-3-aminofuran (4·2), or 3-amino-2-furaldehyde (5·4), ref.[5]. From both tautomeric forms the amino one was backed by the integral curve showing 2 H. The same conclusion favoured also the IR spectrum[1]. Consequently, derivative *II* well reacts in acylation (*IIIa*, *IIIb*) and condensation reactions (*X*). Signal of the —NH— group in *IIIa* and *IIIb* is seen at 9·15 and 10·25, respectively. Substitution of hydrogen by a nitro group in the neighbourhood of amino group (derivative *VIII*) is associated with the change in the chemical shift of the free amino group to 8·22 (s). Ethyl 4-nitro-5-amino furoate does not react with aldehydes under formation of azomethine derivatives due to a lowered electron density at the amino

group[2]. When studying how the position of the —NH— proton signal is influenced by substitution to the adjacent position one learns that besides of electronic also steric effects are involved, as specified in Table I.

The UV spectra of aminofuran derivatives partly reflect the participation of the lone electron pair at nitrogen in conjugation with the π system of furan ring. This conjugation is influenced, in addition to electronic, also by steric effects; thus, λ_{max} of *I* is 293 nm, whereas that of *II* 316 nm. Acetylation fully suppresses entering the electron pair of nitrogen into conjugation, this being documented by the λ_{max} value of *IIIa* (292 nm). Substitution by NO_2 group in position adjacent to amino group leads, however, to a more pronounced conjugation. This fact is demonstrated by λ_{max} 336 nm of derivative *VIII*. The relation of λ_{max} on various substituents Z at position 4 with respect to *IIIa* is exemplified by $\Delta\lambda_{max}$ values listed in Table I. The IR absorption bands (ν_{max} in KBr) were ascribed to the individual functional groups; values of the free —NH_2 group well agree with those published[5].

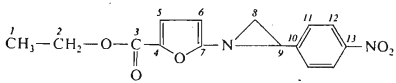
The ^{1}H-NMR spectrum of aziridine derivative *XI* evidences that only one isomer was formed in the reaction. Hydrogens H_1-H_3 of the aziridine ring reveal an ABX pattern; signal of H_1 proton is split by a *trans*-interaction with proton H_3 to a doublet ($J_{1,3} = 4{\cdot}2$ Hz), that of proton H_2 by a *cis*-interaction with proton H_3 also to a doublet ($J_{2,3} = 6{\cdot}8$ Hz). The geminal interaction $J_{1,2} < 1$ Hz, ref.[6], and therefore, proton H_3 is split by *trans* and *cis*-interactions with protons H_1 and H_2 to a doublet of doublets. The structure of derivative *XI* was verified by ^{13}C-NMR spectrum. Chemical shifts of the individual carbon atoms C_1 to C_{13} were ascribed by analogy with the reported data[7–9] of closely related compounds.

Mass spectra of all synthesized derivatives, excepting *IIIb*, *VIIc*, *IX* and *X* served for identification of the particular derivatives. Fragmentation pattern and relative intensities of fragments are presented in the experimental section.

TABLE I

Difference in Chemical Shift of $-NH-COCH_3$ Group $\Delta\delta$(ppm) and $\Delta\lambda_{max}$(nm) of Ethyl 5-Acetylamidofuroate (*IIIa*) Caused by Substituent Z in Position 4

Compound	Z	δ(—NH—)	$\pm\Delta\delta$ ppm	λ_{max}	$\pm\Delta\lambda_{max}$ nm
VI	—NH_2	10·20	1·05	313	21
IX	—N=CH—C_6H_5	10·16	1·01	315	23
VIII	—NO_2	9·76	0·61	333	41
VIIb	—$NHCOCH_3$	9·21	0·06	293	1
IIIa	—H	9·15	0·00	292	0
IV	—Br	8·25	0·90	271	21
VIIc	—$NHCOCCl_3$	7·40	1·75	—	—



XI

EXPERIMENTAL

Melting points were measured on a Kofler block, spectra were recorded with following apparatuses: ^{1}H-NMR spectra with a Tesla BS 487 C (80 MHz), ^{13}C-NMR spectra with a JEOL FX-60 operating at 15·04 MHz in hexadeuteriodimethyl sulfoxide at 22°C (reading accuracy ±1·22 Hz), mass spectra with an AEI MS 902 S, IR spectra with a UR-20 (Zeiss, Jena) in KBr and UV spectra with a Specord UV VIS (Zeiss, Jena) in methanol.

Ethyl 5-Nitrofuroate (*I*)

A mixture consisting of fuming nitric acid (104 g, $d = 1{\cdot}51$) and concentrated sulfuric acid (7 g, $d = 1{\cdot}83$) was dropwise added to acetic anhydride (168 g) at −10°C. Under continuous stirring a solution of ethyl furoate (42 g, 0·3 mol) in acetic anhydride (62 g) was added at −20 to −30°C to this mixture and this temperature was kept for additional 1 h. This mixture was poured on crushed ice (600 g), neutralized with pyridine and gradually heated to 50°C; after 10−15 min of heating at this temperature the solution was cooled, the separated crystals suction filtered, several times washed with water and crystallized from ethanol. Yield 80−90%, m.p. 100−101°C. IR spectrum (KBr) ν_{max}, cm^{-1}: 1732 (C=O), 1542 (C=C), 1500 and 1360 (NO_2), 1015 (C—O—C)$_{fur}$. UV spectrum (methanol) λ_{max}, nm (log ε): 213 (4·16), 293 (4·15). Mass spectrum *m/e* (rel. intensity, %): 185 (47) $C_7H_7NO_5$ M^+, 157 (74), 141 (37), 140 (100), 124 (20), 99 (49), 96 (31), 94 (13), 82 (13), 81 (17), 80 (86,) 68 (11), 66 (26), 54 (23), 53 (29), 52 (17), 45 (40), 44 (40), 43 (11), 39 (20), 38 (71).

Ethyl 5-Aminofuroate (*II*)

The title product was prepared according to[1] in 50−60% yield, m.p. 96°C. For $C_7H_9NO_3$ (155·1) calculated: 9·03% N; found: 9·10% N. IR spectrum (KBr) ν_{max}, cm^{-1}: 3415, 3333, 3240, 1634 (NH_2), 1685 (C=O), 1542 (C=C), 1020 (C—O—C)$_{fur}$. UV spectrum (methanol) λ_{max} nm (log ε): 206 (3·68), 316 (4·28). ^{1}H-NMR spectrum (hexadeuterioacetone): 6·97 d (H_3); 5·10 d (H_4), $J_{3,4} = 4{\cdot}0$ Hz; 5·70 s (—NH_2); 4·11 q (—OCH_2—); 1·19 t (—OCH_2—CH_3). Mass spectrum *m/e* (rel. intensity, %): 155 (60) M^+, 127 (38), 111 (12), 110 (51), 83 (100), 82 (19), 81 (35), 80 (14), 71 (32), 55 (23), 54 (70), 53 (35), 52 (22), 44 (18).

Ethyl 5-Acetylamidofuroate (*IIIa*), ref.[4]

This product was obtained in a 95% yield, m.p. 177°C. IR spectrum (KBr) ν_{max}, cm^{-1}: 3405, 3208, 1595 (—NH_2), 1728 and 1670 (C=O), 1555 (C=O), 1030 (C—O—C)$_{fur}$, 945 and 755 (=C—H). UV spectrum (methanol) λ_{max}, nm (log ε): 207 (3·69), 292 (4·35). ^{1}H-NMR spectrum ($CDCl_3$): 7·11 d (H_3); 6·43 d (H_4), $J_{3,4} = 4{\cdot}0$ Hz; 9·15 broad s (—NH—); 2·12 s (CH_3CO—); 4·25 q (—OCH_2—); 1·27 t (—OCH_2—CH_3). Mass spectrum *m/e* (rel. intensity, %): 197 (19) $C_6H_{11}NO_4$ M^+, 156 (6), 155 (100), 152 (9), 127 (30), 111 (7), 110 (23), 83 (48), 81 (21), 80 (13), 54 (8), 53 (16), 52 (9), 43 (60).

Ethyl 5-Trifluoroacetylamidofuroate (*IIIb*)

Substance *II* (1·55 g, 10 mmol) was refluxed with a 2—3 mol excess of trifluoroacetic acid in xylene (10 ml). The desired product crystallized after cooling in 30—40% yield; m.p. 99°C (sublimation). For $C_9H_8F_3NO_4$ (251·2) calculated: 43·04% C, 3·21% H, 5·58% N; found: 43·40% C, 3·30% H, 5·51% N. IR spectrum KBr λ_{max}, cm^{-1}: 3405, 3240, 1575 (—NH—), 1735 and 1718 (C=O), 1535 (C=C), 1158 (—CF_3), 1027 (C—O—C)$_{fur}$, 970 and 768 (=C—H). ^{1}H-NMR spectrum ($CDCl_3$): 7·22 d (H_3); 6·67 d (H_4), $J_{3,4}$ = 4·0 Hz; 10·25 broad s (—NH—); 4·33 q (—O—CH_2—); 1·35 t (—OCH_2—CH_3).

Ethyl 4-Bromo-5-acetylamidofuroate (*IV*)

Bromine (4·9 g, 30 mmol) in glacial acetic acid (10 ml) was dropwise added during 10—15 min to *IIIa* (6·0 g, 30 mmol) in glacial acetic acid (30 ml); after 20 min the solution was poured into stirred cold water (60 ml). The separated crystals were suction-filtered, washed with water, dried and crystallized from CCl_4. Yield 4·5 g (53%), m.p. 115—117°C. For $C_9H_{10}BrNO_4$ (276·1) calculated: 39·15% C, 3·65% H, 5·07% N, 28·94% Br; found: 38·27% C, 3·57% H, 4·80% N, 30·48% Br. IR spectrum (KBr) ν_{max}, cm^{-1}: 3220, 3172, 1622 (—NH—), 1749 and 1696 (C=O), 1548 (C=C), 1025 (C—O—C)$_{fur}$, 958 and 765 (=C—H). UV spectrum (methanol) λ_{max}, nm (log ε): 206 (4·00), 271 (4·07). ^{1}H-NMR spectrum ($CDCl_3$): 7·09 s (H_3), 8·25 broad s (—NH—), 2·07 s (CH_3CO—), 4·26 q (—O—CH_2—), 1·27 t (—OCH_2—CH_3). Mass spectrum *m/e* (rel. intensity,%): 277, 275 (7); 235, 233 (100); 207, 205 (27); 190, 188 (10); 163 (23), 161 (30), 160 (9), 159 (10), 158 (8), 54 (22), 53 (8), 52 (35) 44 (10) 43 (90).

Ethyl 4-Nitro-5-acetylamidofuroate (*V*)

Fuming nitric acid (50 g, d = 1·51) was slowly added at −10°C to a stirred acetic anhydride (100 g). Powdered *IIIa* was added in small portions at −15 to −20°C and after 10—20 min the reaction mixture was poured onto ice and the separated product suction-filtered. The mean yield was 70%; m.p. 138°C (ethanol). IR spectrum (KBr) ν_{max}, cm^{-1}: 3408, 3129, 1618 (—NH—), 1755 and 1722 (C=O), 1592 (C=C), 1518 and 1341 (NO_2), 1020 (C—O—)$_{fur}$, 955 and 762 (=C—H). UV spectrum (methanol) λ_{max}, nm (log ε): 215 (4·12), 275 (14), 333 (3·77). ^{1}H-NMR spectrum ($CDCl_3$): 7·50 s (H_3), 9·76 broad s (—NH—), 2·37 s (CH_3—CO—), 4·33 q (—O—CH_2—), 1·30 t (—OCH_2—CH_3). Mass spectrum *m/e* (rel. intensity, %): 242 (7) C_9H_{10}·N_2O_6 M^+, 200 (57), 172 (11), 155 (10), 129 (9), 83 (7), 53 (8), 52 (26), 46 (23), 45 (38), 44 (23), 42 (100), 30 (6), 29 (23).

If nitration was carried out for 1—2 h, unidentified products, which undergo spontaneous decomposition, were formed.

Ethyl 4-Amino-5-acetylamidofuroate (*VI*), ref.[3]

The title product was obtained in 50—60% yield; m.p. 162°C. IR spectrum (KBr) ν_{max}, cm^{-1}: 3373—3119, 1667 (—NH—, —NH_2), 1728 and 1689 (C=O), 1558 (C=C), 1024 (C—O—C)$_{fur}$, 970 and 764 (=C—H). UV spectrum (methanol) λ_{max}, nm (log ε): 229 (4·02), 313 (4·01). ^{1}H-NMR spectrum (hexadeuteriodimethyl sulfoxide and hexadeuterioacetone): 6·80 s (H_3), 10·20 broad s (—NH—), 3·90 broad s (—NH_2), 1·96 s (CH_3—CO—), 4·13 q (—O—CH_2—), 1·17 t (—OCH_2—CH_3). Mass spectrum *m/e* (rel. intensity, %): 212 (24) $C_9H_{12}N_2O_4$ M^+, 171 (9), 170 (100), 169 (6), 142 (33), 141 (20), 125 (8), 98 (14), 97 (7), 96 (13), 95 (43), 70 (7), 69 (13), 68 (9), 53 (6), 52 (6), 44 (9), 43 (43), 42 (7), 41 (24), 40 (6).

Ethyl 4-Formylamino-5-acetylamidofuroate (*VIIa*)

Derivative *VI* (2·12 g, 10 mmol) was refluxed with formic acid (99%, 41 ml) and a few drops of HCl for 1 h. Water (20 ml) and charcoal were added, heated to boiling temperature, filtered and evaporated to dryness.The residue was chromatographed on alumina (according to Brockmann, activity grade II) with chloroform–ethanol. First fractions gave *VIIa*, m.p. 174–175°C in a 52% yield. IR spectrum (KBr) ν_{max}, cm^{-1}: 3220, 3158, 1598 (—NH—), 1720 and 1627 (C=O), 1553 (C=C), 1028 (C—O—C)$_{fur}$, 953 and 752 (=C—H). UV spectrum (methanol) λ_{max}, nm (log ε): 220 (4·26), 293 (4·07). Mass spectrum *m/e* (rel. intensity, %): 240 (16), 199 (10), 198 (100), 183 (7), 170 (13), 169 (8), 153 (15), 142 (9), 141 (22), 126 (9), 124 (23), 113 (8), 96 (10), 95 (27), 69 (6), 68 (20), 57 (9), 44 (10), 43 (73), 42 (7), 41 (12), 40 (7).

Ethyl 4,5-Bis(acetylamido)furoate (*VIIb*)

Substance *VI* (1 g, 4·6 mmol) was refluxed in acetic anhydride (10 ml) for 1 h. The desired product crystallized after cooling; yield 0·62 g (52%), m.p. 205°C (ethanol). IR spectrum (KBr) ν_{max}, cm^{-1}: 3260, 3155, 1665 (—NH—), 1742 and 1685 (C=O), 1540 (C=C), 1028 (C—O—C)$_{fur}$, 962 and 763 (=C—H). UV spectrum (saturated methanolic solution) λ_{max}, nm: 220, 293. ^{1}H-NMR spectrum (DMSO—d_6—$CDCl_3$): 7·67 s (H_3), 11·00 s (—NH—), 9·21 s (—NH—), 2·07 s (CH_3CO—), 2·00 s (CH_3CO—), 4·21 q (—O—CH_2—), 1·26 t (—OCH_2—CH_3). Mass spectrum *m/e* (rel. intensity, %): 254 (21) $C_{11}H_{14}N_2O_5$ M^+, 213 (11), 212 (100), 170 (51), 169 (21), 167 (6), 142 (15), 141 (19), 138 (13), 95 (34), 69 (14), 44 (7), 43 (89), 42 (6), 41 (6), 29 (8).

Ethyl 4-Trichloroacetylamido-5-acetylamidofuroate (*VIIc*)

Derivative *VI* (0·5 g, 2·3 mmol) and trichloroacetic acid (0·4 g, 2·4 mmol) were refluxed in acetonitrile (30 ml) with some drops of benzene for 6 h. The mixture was evaporated and the residue crystallized from tetrahydrofuran. The yellow product, m.p. 195–197°C, obtained in a low yield contained, according to analysis, impurities. ^{1}H-NMR spectrum in hexadeuteriоacetone was in accordance with the structure. ^{1}H-NMR spectrum (hexadeuteriоacetone): 7·31 s (H_3), 11·47 broad s (—NH—), 7·40 broad s (—NH—), 2·46 s (CH_3CO—), 4·22 q (—O—CH_2—), 1·22 t (—OCH_2—CH_3).

Ethyl 4-Nitro-5-aminofuroate (*VIII*), ref.[4]

Compound *V* (15 g) in hydrochloric acid (1%, 1500 ml) was refluxed for 1 h. The yellowish crystals, which separated after cooling in a 83% yield had m.p. 150°C. IR spectrum (KBr) ν_{max}, cm^{-1}: 3419, 3312, 3263, 1700 (—NH_2), 1721 (C=O), 1585 (C=C), 1465 and 1288 (NO_2), (C—O—C)$_{fur}$, 958 and 765 (=C—H). UV spectrum (methanol) λ_{max}, nm (log ε): 222 (3·96), 285 (4·23), 336 (4·23). ^{1}H-NMR spectrum (hexadeuteriоacetone): 7·35 s (H_3), 8·22 broad s (—NH_2), 4·21 q (—O—CH_2—), 1·22 t (—OCH_2—CH_3). Mass spectrum *m/e* (rel. intensity,%): 200 (93) $C_7H_8N_2O_5$ M^+, 172 (28), 156 (8), 155 (22), 128 (21), 126 (12), 125 (9), 111 (10), 98 (17), 97 (14), 84 (7), 83 (12), 81 (9), 70 (21), 69 (17), 53 (36), 52 (100), 44 (17), 30 (17), 29 (58).

Ethyl-4(Benzylideneamino)-5-acetylamidofuroate (*IX*)

Ethanolic solution of benzaldehyde (5 mmol in 30 ml) was added to a stirred ethanolic solution of *VI* (5 mmol) and refluxed for 10 min. The product separated in a 90% yield after cooling; m.p. 166°C. IR spectrum (KBr) ν_{max}, cm^{-1}: 3250, 3180, 1632 (—NH—), 1718 and 1695 (C=O),

1 560 (C=C), 1 028 (C—O—C)$_{fur}$, 971, 768 and 700 (=C—H). UV spectrum (methanol λ_{max}, nm (log ε): 200 (4·44), 222 (4·33), 258 (4·30), 315 (4·30). ^{1}H-NMR spectrum (DMSO-d_6–acetone-d_6): 7·60 s (H_3), 10·16 broad s (—NH—), 8·72 s (—N=CH—), 2·02 s (CH_3CO—), 4·21 q (—O—CH_2—), 1·21 t (—OCH_2—CH_3), 7·82–7·42 complex m (H_{phenyl}). Mass spectrum *m/e*: 300 $C_{16}H_{16}N_2O_3$ M^+.

Ethyl 5-(4-Nitrobenzylideneamino)furoate (*X*)

4-Nitrobenzaldehyde in a small excess was added to a solution of *II* (1·5 g, 10 mmol) in ethanol (20 ml) and the mixture was refluxed for 1 h. The residue after evaporation was purified on a silica gel (150/250) column. The yellow product was obtained in a 43% yield; m.p. 157–160°C. For $C_{14}H_{12}N_2O_5$ (288·3) calculated: 58·33% C, 4·19% H, 9·72% N; found: 58·30% C, 4·12% H, 9·78% N. IR spectrum (KBr): ν(—CH=N—) 1 604 cm^{-1}. UV spectrum (methanol) λ_{max}, nm (log ε): 371 (4·17).

1-(5-Ethoxycarbonyl-2-furyl)-2-(4-nitrophenyl)aziridine (*XI*)

A solution of diazomethane (0·8 g) in ether (90 ml) was added to a solution of azomethine *X* (1 g, 3·4 mmol) in tetrahydrofuran. The solution was left to stand for 14 days, impurities were filtered off and *XI* was crystallized from acetone. Yield 0·43 g (41·3%), m.p. 135°C. For $C_{15}H_{14}.N_2O_5$ (302·3) calculated: 59·59% C, 4·66% H, 9·26% N; found: 59·77% C, 4·77% H, 9·25% N. IR spectrum (KBr) ν_{max}, cm^{-1}: 3 129, 2 982, 1 217, 1 170 and 1 037 (aziridine ring), 1725 (C=O), 1 608 (C=C), 1 522 and 1 353 (NO_2), 1 025 (C—O—C)$_{fur}$, 1 004, 965, 849, 765 and 710. UV spectrum (methanol) λ_{max}, nm (log ε): 205 (4·12), 214 (4·05), 288 (4·35). ^{1}H-NMR spectrum (DMSO-d_6): 2·57 d (H_1); 2·80 d (H_2), $J_{1,2} < 1$ Hz; 3·64 dd (H_3), $J_{1,3} = 4{\cdot}2$ Hz (*trans*-interaction), $J_{2,3} = 6{\cdot}8$ Hz (*cis*-interaction); 7·13 d (H_4), 5·96 d (H_5), $J_{4,5} = 3{\cdot}7$ Hz; 7·58 d (H_6); 8·16 d (H_7), $J_{6,7} = 8{\cdot}8$ Hz; 4·18 q (—O—CH_2—); 1·20 t (—OCH_2—CH_3). ^{13}C-NMR (δ, ppm; for, numbering see formula *XI*): 14·24 (C_1), 60·21 (C_2), 163·35 (C_3), 145·41 (C_4), 123·64 (C_5, C_{12}), 120·72 (C_6), 146·95 (C_7), 41·77 (C_8), 95·54 (C_9), 138·10 (C_{10}), 127·54 (C_{11}), 123·64 (C_{12}), 157·50 (C_{13}). Mass spectrum *m/e* (rel. intensity, %): 302 (18), 150 (10), 149 (100), 119 (38), 103 (22), 91 (19), 77 (33), 51 (10), 44 (26), 39 (8).

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