A CONVENIENT SYNTHESIS OF 2,13- AND 3,13-OCTADECADIENYL ACETATES, SEX PHEROMONE COMPONENTS OF THE *Synanthedon* SPECIES

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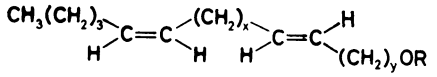
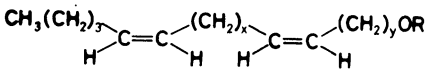
The sex pheromone components of several *Synanthedon* species, 2,13- and 3,13- octadecadienyl acetates (*Ic*, *Id*, *IIc*, *IId*), have been synthesized following the acetylenic route of chain elongation. Starting from ω-alkyn-1-ols *III*, the final compounds were constructed in five steps in about 30% overall yields. Transformation of triple bond containing intermediates into the corresponding (*Z*)- and (*E*)-olefins was achieved either by hydrogenation over the P2-Ni catalyst or by using a dispersion of sodium in toluene. The title pheromones were generated in more than 97% stereoisomeric purity. ^{1}H and ^{13}C NMR data of all derivatives are included.

Since 1974, (3*Z*,13*Z*)-3,13- and (3*E*,13*Z*)-3,13-octadecadienyl acetates (*Ic* and *IIc*) are known as major pheromone components of several *Synanthedon* (*Sessidae*) species[1]. Thereafter, biological activity of some other octadecadienyl acetate isomers has been discovered[2]. Among them, the (2*E*,13*Z*)-2,13-isomer (*Id*) seems to play a very important role because of its pheromonal activity not only towards the *Synanthedon* species (e.g. *S. tipuliformis*)[3] but also towards the other serious pest of fruit trees, *Zeuzera pyrina* L. (*Cossidae*)[4]. Therefore, a simple synthetic procedure common for both *I* and *II* and affording gram quantities required for field tests could be of some importance.



I



II

In formulae *I*, *II*: *a*, x = 8; y = 2; R = H *b*, x = 9, y = 1; R = H
c, x = 8; y = 2; R = $COCH_3$ *d*, x = 9; y = 1; R = $COCH_3$

So far, several multistep syntheses of both *I* and *II* have been reported, including (i) the acetylenic route using two alkylation steps of sodium 1-alkynylide with alkyl iodide in liquid ammonia[1], (ii) Grignard coupling reaction via (*Z*)-3-hexene[5] or (*Z*)-3-octene[6], (ii) use of cuprates[7,8], (iv) Wittig olefination[9,10], and (v) selective 2,ω- to 3,ω-diyn-1-ol isomerization[11]. Most of these methods, however, suffer from some disadvantages, e.g. low stereoselectivity[9,10], or are restricted to only one positional isomer[5-8,11].

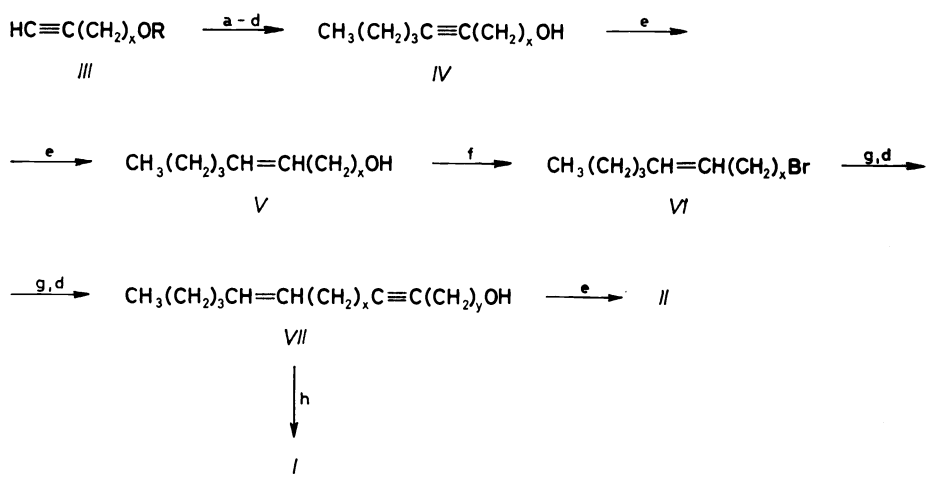
We now report an alternative five-step synthesis of *I* and *II* which proceeds with reasonably good yields in all steps and provides an important extension to the known methodology that it allows *1*) the use of ω-alkyn-1-ols *III* (which are readily available either by alkylation of acetylene with ω-bromoalkan-1-ols[12,13] or, even better, by in situ alkylation of the dianion derived from tetrahydrofurfuryl chloride with alkyl bromides followed by a zipper reaction[14,15]) as the starting material; *2*) the preparation of desired pheromones in high (more than 97%) isomeric purity; and *3*) the use of a common general scheme for the synthesis of both *I* and *II*. The overall route is outlined in Scheme 1.

The four-carbon homologation of the ω-alkyn-1-ols *III* was achieved by alkylating the protected anion with 1-bromobutane. After deprotection with Dowex W-50 (H^+ form) in methanol, the alkynols *IVa* and *IVb* were isolated in 80 and 82% yield, respectively. Hydrogenation of the alkynols *IV* over P2-Ni catalyst[16] gave the (*Z*)--enols *V* in isomeric purity of 98·8% (GC).

Treatment of the (*Z*)-enols *Va* and *Vb* with carbon tetrabromide and triphenylphosphine[17] furnished the corresponding bromides *VIa* and *VIb* in 87% yield. Subsequent alkylation of the anions derived from protected 2-propyn-1-ol and 3-butyn-1-ol (both compounds are commercially available) with *VIa* and *VIb* produced, after deprotection, enyn-1-ols *VIIa* and *VIIb* in moderate yields (about 60%). Based on this, cuprous iodide catalyzed reaction of the Grignard reagent[18] was alternatively used instead of the classical lithium amide procedure but without any improvement in the yields of isolated products.

Partial reduction of enyn-1-ols *VIIa* and *VIIb* was performed using either P2-Ni catalyst as mentioned above or a sodium dispersion in toluene and 1,2-ethanediol[6]. In the first case, the hydrogenation takes place quantitatively with high degree of stereoselectivity; the (*E*,*Z*)-isomer content of the (*Z*,*Z*)-dienols *IIa* and *IIb* was found to be less than 1·4%. In the second case, the (*E*,*Z*)-dienols *Ia* and *Ib* were isolated in the yields of 66% and 73% respectively, the (*Z*,*Z*)-isomer content not exceeding 2·1%. Although the transformation *VIIb* → *Ib* was best accomplished (83% yield) with lithium alanate in tetrahydofuran and diglyme[19], this reduction process does not seem to be of general validity. Attempts to transform similarly *VIIa* to *Ia* were unsuccessful as the reduction was not complete even after 60 h of heating.

Finally, the dienols *Ia*, *Ib*, *IIa* and *IIb* were acetylated with acetic anhydride to afford the pheromones *Ic*, *Id*, *IIc* and *IId*.



In formula *III*: *a*, x = 8; R = H *b*, x = 9; R = H *c*, x = 8; R = ethoxyethyl
d, x = 9; R = ethoxyethyl

In formulae *IV*–*VI*: *a*, x = 8 *b*, x = 9

In formulae *I*, *II*, *VII*: *a*, x = 8; y = 2 *b*, x = 9; y = 1

a: ethyl vinyl ether, *p*-toluenesulfonic acid (TsOH), ether; b: lithium amide, NH_3(l); c: 1-bromobutane, THF; d: Dowex W-50 (H^+ form), MeOH; e: H_2, P2-Ni, EtOH; f: triphenylphosphine, CBr_4, CH_2Cl_2; g: hexamethylphosphoramide (HMPA), $LiC{\equiv}C(CH_2)_yOTHP$; h: Na, toluene, 1,2-ethandiol

SCHEME 1

EXPERIMENTAL

The H^1 and ^{13}C NMR spectra were recorded on an FT-NMR spectrometer Varian XL-200 (at 200·01 and 50·31 MHz) in deuteriochloroform using tetramethylsilane as internal reference. The chemical shifts and coupling constants were obtained by the analysis of the first order spectra. The NMR data are given in Tables I—VI. Gas chromatographical analyses were performed on a HP 5880 A instrument equipped with a flame ionization detector and a 25 m capillary column (internal diameter 0·3 mm, HP5 — 5% phenyl methylsilicon, cross-linked). Column chromatography separations were made on Merck 60 silica gel (0·040—0·063 mm) using a Büchi B-680 Prep LC System. The eluent, light petroleum b.p. 40—60°C with stepwise gradient of ethyl acetate (0; 0·5; 1; 5; 10; 20 and 40%) was delivered by a metering pump at the rate of 40 ml/min at the rate of 40 ml/min for 26·5 mm i.d. columns and 60 mol/min for 38·5 mm i.d. columns.

1-(1-Ethoxyethykoxy)-9-decyne (*IIIc*)

Ethyl vinyl ether (68·5 g, 0·95 mol) was added dropwise to stirred solution of the alcohol *IIIa* (80·0 g, 0·518 mol) and *p*-toluenesulfonic acid (150 mg) in dry ether (500 ml) at 0—3°C. After stirring for 5 h at the same temperature, powdered potassium hydroxide (2·0 g) and water (5 ml)

were introduced. The mixture was then diluted with ether (200 ml) washed with a saturated solution of sodium hydrogen carbonate, brine and dried over potassium carbonate. Evaporation of the solvent and distillation afforded 100·0 g of *IIIc* (85%, b.p. 100—103°C/0·4 kPa).

1-(1-Ethoxyethyloxy)-10-undecyne (IIId) was synthesized analogously from the alcohol *IIIb* (28·0 g, 0·167 mol) and ethyl vinyl ether (24·1 g, 0·334 mol). Yield 36·0 g (90%, b.p. 111—113°C/0·4 kPa).

9-Tetradecyn-1-ol (*IVa*)

To a suspension of lithium amide (prepared from 4·0 g of lithium and 800 ml of liquid ammonia) 100·0 g of *IIIc* (0·442 mol) in tetrahydrofuran (200 ml) was introduced. After stirring for 1·5 h 1-bromobutane (88·2 g, 0·6 mol) in dry tetrahydrofuran (200 ml) was added dropwise and stirring was continued for 4 h. Ammonia was evaporated on standing overnight and the residue was decomposed with ice-cold water. The mixture was then extracted with ether (5 × 500 ml), the ethereal extracts were washed with brine and dried over potassium carbonate. Evaporation of the solvent furnished 121·5 g of a yellow oil. This oil dissolved in methanol (1 500 ml) was treated with Dowex W-50 (H^+ form; 20·0 g) for 20 h. The ion-exchanger was filtered off and the solvent removed in vacuo. Distillation of the residue gave 72·7 g of *IVa* (80%), b.p. 136 to 140°C/0·3 kPa.

10-Pentadecyn-1-ol (IVb) was synthesized analogously from *IIId* (36 g, 0·15 mol), lithium (1·25 g) and 1-bromobutane (24·6 g, 0·18 mol). Yield 27·3 g (81%), b.p. 150—152°C/0·3 kPa.

Hydrogenation of alkynols *IVa* and *IVb* to (*Z*)-alkenols *Va* and *Vb*

1,2-Diaminoethane (3·2 g) and alkynol *IV* (0·014 mol) were added to a suspension of P2-Ni (refs[16,20]) (prepared from 1·98 g of nickel(II) acetate) in ethanol (90 ml). The hydrogenation was monitored of the solution by GLC. The crude products were purified by vacuum distillation. The colorless oily products were thus obtained in yields of about 93—95%, in isomeric purity higher than 98·5% (*Z*)-9-Tetradecen-1-ol (*Va*) from *IVa*; b.p. 128—130°C/0·3 kPa. (*Z*)-10-Pentadecen-1-ol (*Vb*) from *IVb*; b.p. 138—140°C/0·3 kPa.

1-Bromo-(*Z*)-9-tetradecene (*VIa*)

Triphenylphosphine (53·0 g, 0·202 mol) in dichloromethane (200 ml) was added dropwise to a solution of *Va* (40·0 g, 0·188 mol) and tetrabromomethane (70·0 g, 0·211 mol) in dichloromethane (400 ml) at 0—3°C. The mixture was warmed to 20°C over 1 h. After stirring for 14 h the solvent was removed on a rotary evaporator and light petroleum (300 ml) was added to the residue. The mixture was cooled to 0°C and filtered. The solid residue was washed with ice-cold light petroleum and the filtrate was concentrated in vacuo. The crude residue was purified by column chromatography (silica gel, benzene) and distilled under vacuum. The bromide *VIa* was obtained as a colorless oil (45·8 g, 89%), b.p. 150—153°C/0·4 kPa.

1-Bromo-(Z)-10-pentadecene (VIb). In the same manner as described above, *Vb* (20·0 g, 0·088 mol) was brominated with tetrabromomethane (39·2 g, 0·118 mol) and triphenylphosphine (27·2 g, 0·102 mol) to give 21·7 g (85%) of *VIb*, b.p. 140—142°C/0·2 kPa.

(*Z*)-13-Octadecen-3-yn-1-ol (*VIIa*)

Butyllithium (1·6M solution in hexane; 15·7 ml; 25 mmol) was added to a stirred solution of

1-(2-tetrahydropyranyloxy)-3-butane (4·63 g, 30 mmol) in tetrahydrofuran (30 ml) and HMPA (10 ml) at −20°C under nitrogen. After 1 h, bromoalkene *VIa* (5·0 g, 18·1 mmol) in HMPA (10 ml) was added dropwise and the mixture was stirred for 4 h at room temperature. The solution was then poured into ice-cold water, and extracted with light petroleum. After evaporation of the solvent the yellow residue was dissolved in methanol (100 ml) and treated with Dowex W-50 (H^+ form, 2 0 g) for 16 h .The mixture was filtered, the extract dried over $MgSO_4$ and evaporated to dryness in vacuo. Purification of the crude product by column chromatography (silica gel; toluene) gave 2·91 (61%) of *VIIa*.

(Z)-*13-Octadecen-2-yn-1-ol* (VIIb). In the same manner as described above, *VIb* (8·68 g, 30 mmol) was treated with 1-(2-tetrahydropyranyloxy)-2-propyne (6·3 g, 40 mmol) and butyllithium (1·6M solution in hexane; 21·9 ml, 35 mmol) to give 4·76 g (60%) of *VIIb*.

Reduction of enynols *VIIa* and *VIIb* to dienols *Ia*, *Ib*, *IIa* and *IIb*

A) (Z)-*reduction*: Partial hydrogenation of the enynols *VII* was performed using P2-Ni catalyst[16,20]. The reaction was monitored by examining aliquots of the solution by GLC. The crude products were purified by column chromatography (silica gel; light petroleum–ethyl acetate) to give (*Z*,*Z*)-dienols *IIa*, *IIb* in nearly quantitative yields and more than 98·6% geometrical purity as checked by GLC

B) (E)-*reduction*: To a dispersion of sodium (2·0 g, 87 mmol) in toluene (250 ml), the solution of enynol *VII* (17·8 mmol) and 1,2-ethanediol (2·3 g, 37 mmol) in toluene (50 ml) was introduced under nitrogen. After stirring for 2 h, at 98—100°C and subsequent cooling the reaction mixture was neutralized with 12% hydrochloric acid (100 ml). The organic layer was washed with saturated solution of sodium hydrogen carbonate, dried (K_2CO_3) and concentrated in vacuo. The crude product was chromatographed on silica gel eluting with stepwise gradient of ethyl acetate in light petroleum to give about 65—70% yields of (*Z*,*E*)-dienols *Ia* and *Ib*. The isomeric purity of the products was better than 97·9%.

C) (E)-*Reduction using lithium alanate*[19]: To a solution of *VIIb* (3·96 g, 15 mmol) in tetrahydrofuran (125 ml) lithium alanate (2·85 g, 75 mmol) was added at −20°C under nitrogen. After heating for 10 h at 60°C, the mixture was decomposed with cold water (65 ml) and a saturated solution of potassium sodium tartrate (250 ml) and extracted with ether (3 × 400 ml). The etheral extracts were washed with water and dried (K_2CO_3). Removal of the solvent in vacuo and a purification of the residue by column chromatography (silica gel; stepwise gradient of ethyl acetate in light petroleum) afforded 3·3 g (83%) of the (*Z*,*E*)-dienol *Ib* of the same isomeric purity as in *C*). An attempt to reduce *VIIa* by exactly the same procedure did not lead to satisfactory results. Neither the use of higher molar concentrations of lithium alanate, nor prolonged reaction times (up to 60 h) were successful. In all cases the reduction was incomplete.

Acetates *Ic*, *Id*, *IIc* and *IId*

A typical acetylation procedure was as follows. (*Z*,*Z*)-3,13-Octadecadien-1-ol *IIa* (0·3 g, 1·12 mmol) was added to acetic anhydride (1·33 g, 13 mmol) and pyridine (2·04 g, 23 mmol) at −10°C and left in the refrigerator overnight. The mixture was then poured into ice-cold water, extracted with ether, and chromatographed to give an almost quantitative yield of more than 98·5% pure product. No decrease in isomeric purity was observed.

TABLE I

^{1}H NMR chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis) of compound *IV*–*VI* in deuteriochloroform (200·01 MHz, tetramethylsilane as internal standard)

Proton	Compound					
	IVa	*IVb*	*Va*	*Vb*	*VIa*	*VIb*
H-1	3·60 t (2 × 6·6)	3·60 t (2 × 6·6)	3·60 t (2 × 6·6)	3·64 t (2 × 6·6)	3·40 t (2 × 6·9)	3·40 t (2 × 6·9)
H-2 to H-7	1·25— —1·56 m	1·26— —1·50 m	1·23— —1·53 m	1·21— —1·56 m	1·25— —1·56 m	1·25— —1·53 m
H-8	2·12 m	2·16 m	2·00 m		2·02 m	
H-9	—	—	5·24—	2·03 m	5·28—	2·02 m
H-10	—	—	—5·41 m	5·27—	—5·43 m	5·27 m
H-11	2·12 m	2·16 m	2·00 m	—5·44 m	2·02 m	—5·41
H-12	1·25	1·26—	1·23—	2·03 m	1·25—	2·02 m
H-13	—1·56 m	—1·50 m	—1·53 m	1·21—	—1·56 m	1·25—
H-14	0·88 t (2 × 7·1)	0·93 t (2 × 7·2)	0·88 t (2 × 7·0)	—1·56 m	0·90 t (2 × 7·0)	—1·53 m
H-15	—	—	—	0·91 t (2 × 7·1)	—	0·90 t (2 × 7·0)

TABLE II

^{13}C NMR chemical shifts (δ, ppm) of compounds *IV*—*VI* in deuteriochloroform ($CDCl_3$ = = 77·00 ppm as internal standard)

Carbon	Compound					
	IVa	*IVb*	*Va*	*Vb*	*VIa*	*VIb*
C-1	62·39 t	62·94 t	62·93 t	62·84 t	33·99 t	24·04 t
C-2	32·50 t	32·72 t	31·92 t	31·91 t	31·94 t	31·99 t
C-3	25·57 t	25·69 t	25·71 t	25·72 t	28·14 t	28·21 t
C-4	29·20 t	29·44 t	29·19 t	29·23 t	28·72 t	28·79 t
C-5	28·96 t	29·33 t	29·46 t	29·43 t	29·14 t	29·26 t
C-6	28·96 t	29·10 t	29·37 t	29·54 t	29·30 t	29·43 t
C-7	28·62 t	29·04 t	29·70 t	29·40 t	29·68 t	29·43 t
C-8	18·23 t	28·77 t	26·87 t	29·70 t	26·90 d	29·76;t
C-9	79·91 s	18·39 t	129·82 d	26·86 t	129·91 d	26·95 t
C-10	79·91 s	80·13 s	129·76 d	129·77 d	129·74 d	129·91 d
C-11	18·52 t	80·13 s	27·13 t	129·77 d	27·13 t	129·83 d
C-12	31·09 t	18·69 t	32·74 t	27·13 t	32·81 t	27·20 t
C-13	21·73 t	31·22 t	22·29 t	32·72 t	22·33 t	32·87 t
C-14	13·93 q	21·87 t	13·94 q	22·28 t	13·98 q	22·38 t
C-15	—	13·57 q	—	13·92 q	—	14·03 q

TABLE III

^{1}H NMR chemical shifts (δ, ppm) and coupling constants (J, Hz) of compounds *VII* in deuteriochloroform (200·01 MHz, tetramethylsilane as internal standard)

Parameter	Compound			
	VIIa	*VIIb*	*VII*[a]	*VIId*[b]
H-1	3·68 t	4·24 t	4·13 t	4·66 t
H-2	2·43 tt	—	2·49 tt	—
H-4	—	2·20 tt	—	2·21 tt
H-5	2·16 tt		2·13 tt	
H-6 to H-11	1·22— —1·47 m	1·23— —1·57 m	1·24— —1·42 m	1·24— —1·57 m
H-12	2·02 m	2·02 m	2·01 m	2·02 m
H-13 and H-14	5·26— —5·43 m	5·28— —5·40 m	5·29— —5·41 m	5·29— 5·39 m
H-15	2·02 m	2·02 m	2·01 m	2·02 m
H-16 and H-17	1·22— —1·47 m	1·23— —1·57 m	1·24— —1·42 m	1·24— —1·57 m
H-18	0·90 t	0·90 t	0·90 t	0·90 t
J(1, 2)	6·2	—	7·1	—
J(1, 4)	—	2·2	—	2·2
J(2, 5)	2·4	—	2·4	—
J(4, 5)	—	7·0	—	7·1
J(5, 6)	6·9	[c]	6·9	[c]
J(17, 18)	7·1	7·0	7·1	7·0

[a] OAc 2·06 s; [b] OAc 2·09 s; [c] coupling not observed.

TABLE IV

^{13}C NMR chemical shifts (δ, ppm) of compounds *VII* in deuteriochloroform ($CDCl_3$ = = 77·00 ppm as internal standard

Carbon	Compound			
	VIIa	*VIIb*	*VIIc*	*VIId*
C-1	61·37 t	51·33 t	62·92 t	52·83 t
C-2	18·73 t	78·25 s	18·67 t	73·82 s
C-3	76·22 s	86·55 s	75·42 s	87·68 s
C-4	82·83 s	18·70 t	82·08 s	18·72 t
C-5	23·19 t	29·72 t	19·24 t	29·71 t
C-6	29·74 t	29·42 t	29·73 t	29 43 t
C-7	29·41 t	29·42 t	29·41 t	29·43 t
C-8	29·25 t	29·24 t	29·25 t	29·23 t
C-9	29·12 t	29·10 t	29·11 t	29·06 t
C-10	28·98 t	28·85 t	28·88 t	28·81 t
C-11	28·89 t	28·58 t	28·81 t	28·38 t
C-12	26·92 t	26·88 t	26·90 t	26·88 t
C-13	129·82 d	129·80 d	129·82 d	129·80 d
C-14	129·87 d	129·80 d	129·86 d	129·80 d
C-15	27·18 t	27·15 t	27·17 t	27·15 t
C-16	31·96 t	31·93 t	31·95 t	32·56 t
C-17	22·35 t	22·31 t	22·33 t	22·31 t
C-18	14·01 q	13·96 q	13·99 q	13·95 q
C-19	—	—	170·86 s	170·27 s
C-20	—	—	20·90 q	20·76 q

TABLE V

^{1}H NMR chemical shifts (δ, ppm) and coupling constants (J, Hz) of compounds *I* and *II* in deuteriochloroform (200·01 MHz, tetramethylsilane as internal standard)

Parameter	Compound							
	Ia	*Ib*	*Ic*[a]	*Id*[b]	*IIa*	*IIb*	*IIc*[c]	*IId*[d]
H-1	3·65 t	4·08 dt	4·06 t	4·49 bd	3·63 t	4·20 dt	4·06 t	4·61 bd
H-2	2·29 m	5·54—	2·31 m	5·54 m	2·32 m	5·54—	2·37 m	5·51 m
H-3	5·39 m	—5·78 m	5·35 m	5·76 m	5·35 m	—5·67 m	5·35 m	5·65 m
H-4	5·58 m	2·02 m	5·52 m	2·03 m	5·56 m	2·02 m	5·50 m	2·04 m
H-5	2·04 m	1·21—	2·01 m	1·21—	2·03 m	1·22—	2·02 m	1·23—
H-6 to H-11	1·24— —1·47 m	—1·38 m	1·23— —1·40 m	—1·37 m	1·23— —1·41 m	—1·39 m	1·22— —1·41 m	—1·40 m
H-12	2·04 m	2·02 m	2·01 m	2·03 m	2·03 m	2·02 m	2·02 m	2·04 m
H-13 and H-14	5·28— —5·43 m	5·29— —5·40 m	5·29— —5·41 m	5·26— —5·42 m	5·29— —5·41 m	5·28— 5·43 m	5·28— 5·41 m	5·29— 5·40 m
H-15	2·04 m	2·02 m	2·01 m	2·03 m	2·03 m	2·02 m	2·02 m	2·04 m
H-16 and H-17	1·24— —1·47 m	1·21— —1·38 m	1·23— —1·40 m	1·21— —1·37 m	1·23— —1·41 m	1·22— 1·39 m	1·22— 1·41 m	1·23— 1·40 m
H-18	0·92 t	0·90 t	0·90 t	0·89 t	0·89 t	0·90 t	0·89 t	0·90 t
J(1, 2)	6·5	4·9	7·0	6·3	6·5	6·5	7·0	6·4
J(1, 3)	[e]	0·9	[e]	0·7	[c]	0·6	[e]	1·2
J(2, 3)	6·6	[e]	6·5	—15·3	7·2	[e]	7·2	—10·8
J(2, 4)	1·1	[e]	1·1	0·8	1·4	[e]	1·4	1·3
J(3, 4)	—15·3	[e]	—15·3	6·4	—10·9	[e]	—10·9	7·1
J(3, 5)	1·2	[c]	1·0	[e]	1·4	[c]	1·3	[e]
J(4, 5)	6·5	[e]	6·3	[e]	7·2	[e]	7·2	[e]
J(17, 18)	7·1	7·0	7·1	7·1	7·1	7·1	7·1	7·1

[a] OAc 2·04 s; [b] OAc 2·04 s; [c] 2·04 s; [d] 2·06 s; [e] parameter not observed.

TABLE VI

^{13}C NMR chemical shifts (δ, ppm) of compounds *I* and *II* in deuteriochloroform ($CDCl_3$ = = 77·00 ppm as internal standard)

Carbon	Compound							
	Ia	*Ib*	*Ic*	*Id*	*IIa*	*IIb*	*IIc*	*IId*
C-1	62·03 t	63·78 t	63·86 t	65·26 t	62·30 t	58·61 t	63·94 t	60·31 t
C-2	32·66 t	128·75 d	32·60 t	123·63 d	30·78 t	128·26 d	27·27 t	123·19 d
C-3	125·65 d	133·52 d	124·93 d	136·62 d	124·91 d	133·28 d	124·19 d	135·35 d
C-4	134·40 d	32·19 t	133·60 d	27·14 t	133·47 d	27·43 t	132·93 d	27·47 t
C-5	26·91 t	29·73 t	27·19 t	29·71 t	27·35 t	29·75 t	26·79 t	29·70 t
C-6	29·75 t	29·54 t	31·95 t	29·47 t	29·74 t	29·60 t	29·72 t	29·51 t
C-7	29·46 t	29·51 t	29·75 t	29·47 t	29·68 t	29·55 t	29·56 t	29·46 t
C-8	29·46 t	29·46 t	29·48 t	29·40 t	29·48 t	29·52 t	29·47 t	29·41 t
C-9	29·46 t	29·27 t	29·39 t	29·24 t	29·48 t	29·47 t	29·47 t	29·36 t
C-10	29·29 t	29·16 t	29·29 t	29·11 t	29·27 t	29·44 t	29·25 t	29·23 t
C-11	29·18 t	29·11 t	29·12 t	28·83 t	29·27 t	29·28 t	29·25 t	29·14 t
C-12	26·91 t	26·88 t	26·91 t	26·86 t	27·17 t	26·91 t	26·88 t	26·85 t
C-13	129·85 d	129·82 d	129·85 d	129·78 d	129·83 d	129·80 d	129·80 d	129·74 d
C-14	129·85 d	129·82 d	129·85 d	129·78 d	129·83 d	129·85 d	129·80 d	129·74 d
C-15	27·19 t	27·17 t	27·19 t	27·14 t	26·89 t	27·19 t	27·15 t	27·13 t
C-16	31·97 t	31·94 t	31·95 t	31·92 t	31·95 t	31·96 t	31·93 t	31·91 t
C-17	22·34 t	22·32 t	22·35 t	22·89 t	22·32 t	22·34 t	22·31 t	22·28 t
C-18	13·99 q	13·97 q	14·00 q	13·93 q	13·97 q	13·99 q	13·95 q	13·92 q
C-19	—	—	171·09 s	170·76 s	—	—	171·00 s	170·82 s
C-20	—	—	20·98 q	20·94 q	—	—	20·91 q	20·88 q

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