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DITERPENES FROM *HETEROPAPPUS ALTAICUS*

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Key Word Index—*Heteropappus altaicus*, Compositae, diterpenes, clerodane derivatives, *seco*-clerodane, neryl geraniol derivative

Abstract—The aerial parts of *Heteropappus altaicus* afforded, in addition to more widespread compounds and known clerodane derivatives, three new ones and a *seco*-clerodane acid Furthermore, a neryl geraniol derivative was present The structures were elucidated by spectroscopic methods The stereochemistry was solved by NOE difference spectroscopy and by the Horeau method

INTRODUCTION

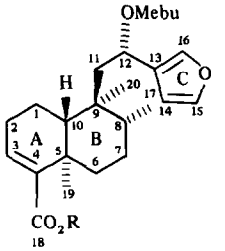
The small East Asian genus *Heteropappus* (Compositae, tribe Astereae) has not so far been studied chemically We have therefore investigated *H altaicus* (Willd) Novopokrov (= *Aster altaicus* Willd) from Mongolia The results are discussed in this paper

RESULTS AND DISCUSSION

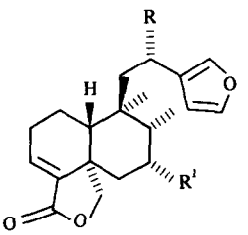
The aerial parts of *Heteropappus altaicus* afforded germacrene D, caryophyllen-1β,10α-epoide, farnesol, 5-*O*-desmethylnobiletin, previously isolated from this species [1], (−)-hardwickiic acid [2], hautriwaic acid [3], the corresponding lactone **3** [4] and five more diterpenes, the clerodanes **1**, **4** and **5**, the *seco* derivative **6** and the neryl geraniol derivative **8**

The identity of (−)-hardwickiic acid with known absolute configuration was established by ^{1}H NMR spectroscopy of the corresponding methyl ester including spin decoupling and NOE difference spectroscopy, which clearly showed the α-orientation of the methyl groups at C-8 and C-9, while the A-ring was in a half-chair conformation with H-1α axially orientated The spectral data and the optical rotations of the hautriwaic acid and its lactone **3** were identical with those of authentic materials

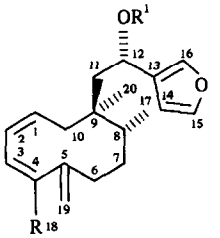
The IR spectrum of **4**, molecular formula $C_{20}H_{26}O_4$, showed the presence of a γ-lactone and a hydroxyl group, while the ^{1}H NMR spectrum (Table 1) clearly indicated a β-substituted furan Furthermore, the spectrum was similar to that of **3** However, the H-12 double-doublets were replaced by a broadened doublet at δ4 88 This clearly indicated that the hydroxyl group was at C-12 This could be supported by spin decoupling Irradiation at δ4 88 collapsed the double-doublets at δ2 01 and 1 77 to geminal coupled doublets (H-11) Furthermore, the presence of a 12-hydroxy derivative of **3** was supported by the downfield shift of the H-14 and H-16 signals, which obviously were induced by the deshielding effect of the oxygen function In the mass spectrum a prominent peak at *m/z* 97 agreed well with a fragment containing the furan moiety with a hydroxymethine group



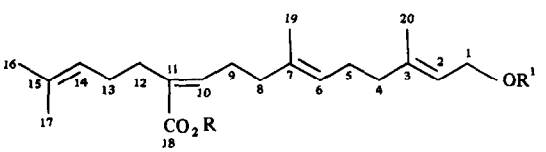
1 R=H
2 R=Me



	R	R^1
3	H	H
4	OH	H
5	OH	OH



	R	R^1
6	CO_2H	Mebu
7	CH_2OH	H



	R	R^1
8	H	H
9	Me	Ac

Table 1 ^{1}H NMR spectral data of compounds **2** and **4**–**7** (400 MHz, $CDCl_3$, TMS as internal standard)

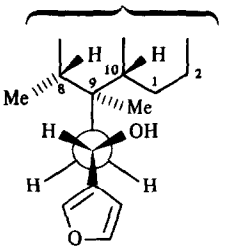
	2*	4	5	6-Methyl ester	7†
H-1α		1 03 *dddd*	1 11 *dddd*	5 22 *br ddd*	5 21 *dddd*
H-1β		2 12 *br d*	2 13 *br d*		
H-2α	2 27 *m*	2 32 m	2 34 m	5 87 *br d*	5 91 *br d*
H-2β		2 26 *m*	2 25 *m*		
H-3	6 59 *br dd*	6 75 *dd*	6 73 *dd*	7 24 *br dd*	5 98 *br s*
H-6α		1 90 *ddd*	2 34 *dd*	2 61 *br d*	2 37 *br d*
H-6β		1 26 *dddd*	1 43 *ddd*	2 05 *br dd*	2 02 *ddd*
H-7α		1 49 *dddd*	—	1 55 *m*	0 84 *m*
H-7β		1 73 *dddd*	4 12 *ddd*		1 56 *m*
H-8	1 87 *ddq*	1 82 *ddq*	1 88 *dq*	1 41 *ddq*	1 34 *ddq*
H-10	2 27 *br d*	2 19 *br d*	2 25 *br d*	2 28 *dd*	2 40 *br dd*
H-10′				1 88 *br d*	1 93 *dddd*
H-11	2 12 *dd*	2 01 *dd*	2 01 *d*	2 09 *dd*	1 81 *dd*
H-11′	1 76 *dd*	1 77 *dd*	1 66 *dd*	1 61 *dd*	1 59 *dd*
H-12	5 89 *dd*	4 88 *br d*	4 84 *dd*	6 01 *dd*	4 92 *dd*
H-14	6 39 *br s*	6 41 *dd*	6 41 *br s*	6 39 *br s*	6 42 *dd*
H-15	7 34 *dd*	7 38 *dd*	7 40 *dd*	7 34 *dd*	7 38 *d*
H-16	7 39 *br s*	7 39 *br s*	7 39 *br s*	7 41 *br s*	
H-17	0 69 *d*	0 79 *d*	0 99 *d*	0 78 *d*	0 76 *d*
H-19	1 24 *s*	3 91 *dd*	3 92 *dd*	5 03 *br s*	4 96 *dd*
H-19′		4 28 *d*	4 28 *d*	4 79 *br s*	4 80 *dd*
H-20	0 70 *s*	0 57 *s*	0 83 *s*	0 72 *s*	0 90 *s*
OMe	3 67 *s*	—	—	3 77 *s*	—
OCOR	2 27 *tq*	—	—	2 30 *ddq*	—
	1 57 *ddq*			1 61 *m*	
	1 38 *ddq*			1 41 *ddq*	
	0 75 *t*			0 79 *t*	
	1 06 *d*			1 08 *d*	

*Remaining signals were overlapped multiplets

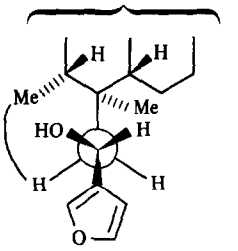
†4 19 *ddd* and 4 08 *d* (H-18)

J (Hz) Compounds **2**, **4**, **5** 1α, 1β = 1α, 2β = 13, 1α, 2α = 4, 1α, 10 = 12, 1β, 2α = 3 5, 1β, 2β ~ 2, 2α, 2β = 18, 2α, 3 = 7, 2β, 3 = 2, 6α, 6β = 13, 6α, 7α = 6α, 7β = 3, 6β, 7α = 12, 6β, 7β = 3 5, 6β, 19α = 2, 7α, 8 = 12, 7β, 8 = 3 5, 8, 17 = 7, 11, 11′ = 16, 11, 12 = 9, 11′, 12 = 3, 14, 15 = 15, 16 ~ 1 5, compound **2** 2α, 3 = 2β, 3 ~ 3, 11, 11′ = 15, 11, 12 = 7, 11′, 12 = 5 5, compound **5** 6α, 7β = 6β, 7β = 7β, 8β ~ 3, compounds **6**-methyl ester and **7** 1, 2 = 1, 10 = 12, 1, 10′ = 4, 1, 3 = 2, 3 = 2, 18 = 3, 18 ~ 1 5, 6α, 6β = 6β, 7α = 13 5, 6β, 7β = 2 5, 7α, 8 ~ 10, 7β, 8 ~ 7, 8, 17 = 7, 11, 11′ = 15, 11, 12 = 9, 11′, 12 = 2 5, (compound **7** 6α, 19 = 6α, 19′ ~ 1 5), OMebu 2′, 3_1′ = 2′, 3_2′ = 3′, 4′ = 2′, 5′ = 7, 3_1′, 3_2′ = 14,

Also the ^{13}C NMR spectrum (see Experimental) agreed well with the proposed structure (**4**) Only the relative configuration at C-12 had to be established Using the Horeau method [5], in addition to the phenyl butyrate of **4**, (−)-2-phenylbutyric acid in an optical yield of 27% was obtained Therefore most likely **4** had a preferred conformation, as already indicated by the differences of the couplings $J_{11\,12}$ and $J_{11',12}$ This was established by NOE difference spectroscopy Clear effects were observed between H-12 and H-8, between OH and H-10, between H-17 and H-11, and between H-7α and H-19 As followed from inspection of a Dreiding model, these results required the given stereochemistry (see **4a**) The configuration and conformation **4b** would require an NOE between H-17 and H-11 (where $J_{11\,12}$ is large) and also the observed NOEs could not be explained Oxidation of **4** using pyridinium dichromate afforded the corresponding 12-oxo derivative, its ^{1}H NMR spectrum also supporting



4a



4b

the structure The ^{1}H NMR data of the phenyl butyrate showed some pronounced differences from those of **4** In addition to the expected downfield shift of the H-12 signal, a shielding effect of the phenyl group was visible,

which led to a clear upfield shift of the signals of the furan protons and even the chemical shifts of the protons of ring A were affected

The molecular formula of **5** indicated that this compound had one additional oxygen function As followed from the fragmentation pattern by the double elimination of water, a diol was present The ^{1}H NMR spectrum (Table 1) was close to that of **4** However, the additional hydroxyl group caused some clear differences The position of the new oxygen function followed from the H-8 signal, which was now a clear doublet quartet, and the deshielding effects on H-17, H-19′ and H-20 Furthermore, these effects clearly showed that an axial hydroxyl group was present As the signals and couplings of H-11 and H-12 were almost the same as those of **4**, the same configuration at C-12 had to be assumed

The structure of **1**, which was isolated as its methyl ester **2**, also followed from the ^{1}H NMR spectrum (Table 1) All signals, except those for H-11 and H-12, were nearly identical to those of the methyl ester of (−)-hardwickiic acid The presence of a 12-methyl butyrate was deduced from the ^{1}H NMR spectral data, while the position of the ester group followed from the chemical shifts of H-11 and H-12 Furthermore, biogenetic considerations supported the proposed identical configuration at C-12, as **4** and **5** surely were formed both from hardwickiic acid as the common precursor

The *seco* compound **6** was isolated as its methyl ester The ^{1}H NMR spectrum (Table 1) was close to that of the corresonding 12-desacyloxy derivative, called strictic acid [6], which is identical to *seco*-nidoresedic acid [7, 8], where however, the configuration at C-9 was not established The presence of an oxygen function at C-12 was also indicated by the ^{1}H NMR data As the signals of H-11 and H-12, as well as those of the ester residue, were close to the corresponding ones of **2**, an identical situation of the side chain was most likely Lithium alanate reduction of the methyl ester afforded the diol **7**, its ^{1}H NMR spectrum further supporting the proposed structure All signals (Table 1) could be assigned by spin decoupling Again, biogenetic considerations led to the assumption that **6** had the same configuration at C-12 as **1**, **4** and **5** The 1,2-dehydro derivative of **1** could be the precursor of **6** A photochemically induced electrocyclic reaction could give an isomeric triene, which could be transformed by a 1,7-H shift to **6**

The ^{1}H NMR spectrum of **9** (Table 2), obtained by esterification and acetylation of the natural compound, clearly showed that a derivative of an alicyclic diterpene with a primary acetoxyl group was present, where one olefinic methyl was transformed to a carbomethoxyl group Accordingly, the position of this function had to be established In the ^{1}H NMR spectrum in $CDCl_3$, several signals were overlapped and therefore conclusive sequence determination by spin decoupling was not possible. However, in deuteriobenzene all signals were separated Accordingly, the whole sequence could be established as the low-field triplet at δ6 95 obviously was that of the proton in the β-position to the carbomethoxyl group This chemical shift further indicated the presence of a carbomethyl-bearing double bond with the *E*-configuration The assignment of H-14 clearly followed from the splitting of the signal at δ5 29 Starting spin decoupling at this point, the signals of H-13, H-16 and H-17 could be assigned As the H-13 signal was coupled with the low-field triplet at δ2 54, obviously that in the α-position to the carbomethoxyl group, the position of the latter was determined Furthermore, a very small allylic coupling between the signals at δ2 54 and 6 95 was present The stereochemistries of the Δ^2- and Δ^6-double bonds were assigned by comparison of the observed chemical shifts with those of similar compounds

Table 2 ^{1}H NMR spectral data of compound **9** (400 MHz, TMS as internal standard)

	In C_6D_6	In $CDCl_3$
H-1	4 66 *br d*	4 58 *br d*
H-2	5 46 *tq*	5 39 *br t*
H-4	1 97 *br t*	2 07 *m*
H-5	2 07 *br dt*	
H-6	5 15 *tq*	5 13 *br t*
H-8	2 01 *br t*	2 07 *m*
H-9	2 21 *dt*	2 25 *dt*
H-10	6 95 *t*	6 72 *t*
H-12	2 54 *t*	2 30 *t*
H-13	2 33 *br dt*	2 07 *m*
H-14	5 29 *tqq*	5 13 *br t*
H-16	1 69 *br s*	1 69 *br s*
H-17	1 62 *br s*	1 59 *br s*
H-19	1 50 *br s*	1 57 *br s*
H-20	1 53 *br s*	1 66 *br s*
OAc	1 74 *s*	2 04 *s*
OMe	3 51 *s*	3 73 *s*

J (Hz) 1, 2 = 5, 6 = 9, 10 = 13, 14 = 7, 2, 20 = 6, 19 = 14, 16 = 14, 17 ~ 1, 4, 5 = 8, 9 = 12, 13 = 7 5

EXPERIMENTAL

The air-dried aerial parts (500 g, collected in the Mongolian Peoples Republic, Tow Aimak, near Telangin-Baischin in July 1983, voucher 60/83 deposited at the Academy of Sciences, Institute of Biochemistry of Plants, Halle, G D R) were extracted with MeOH–Et_2O–petrol (1 1 1) and the extract obtained was worked up in the usual way [9] Fractions obtained by CC (SiO_2) were as follows 1 (petrol), 2 (Et_2O–petrol, 1 9), 3 (Et_2O–petrol, 1 3), 4 (Et_2O–petrol, 1 1, and Et_2O) and 5 (Et_2O–MeOH, 9 1) Fraction 1 gave 3 mg germacrene D (^{1}H NMR, GC/MS) Fraction 2 was purified further by TLC (SiO_2, PF 254, Et_2O–petrol, 1 9) The less polar band gave 3 mg caryophyllen-1β,10α-epoxide (identical with an authentic sample) The main band was esterified by the addition of CH_2N_2 TLC (Et_2O–petrol, 1 20) of this mixture gave, after 2 developments, 40 mg of a compound (R_f 0 5), identical in all respects including optical rotation to the methyl ester of hardwickiic acid Fraction 3 was esterified by addition of CH_2N_2 and the ester mixture was separated by TLC (Et_2O–petrol, 1 3), affording two bands (R_f 0 7 and 0 4) The first part was further purified by TLC on $AgNO_3$-coated SiO_2 (Et_2O–petrol, 1 9) to give 10 mg **2** (R_f 0 41) and 10 mg **6**-methyl ester (R_f 0 20) The second band afforded on repeated TLC (Et_2O–petrol, 1 3, 2 developments) 20 mg of the lactone of hautriwaic acid (**3**) [4] (R_f 0 30) Fraction 4 was separated by medium pressure chromatography (MPC) (60 g SiO_2, ϕ40–60 μm, *ca* 3 bar, 25 ml fractions) Fractions 5–9 (Et_2O–petrol, 1 1) gave 70 mg **6**, which was purified as its methyl ester by TLC (Et_2O–petrol, 1 3, R_f 0 42) Fractions 10–12 (Et_2O) gave 1 3 g farnesol (identical with an authentic sample by

^{1}H NMR and IR) and fractions 13–18 (Et_2O) gave after TLC (Et_2O–petrol, 1 1) 100 mg **4** (R_f 0 41) Fractions 19–25 (Et_2O) gave nothing characteristic and 26–30 (Et_2O) after TLC (Et_2O–petrol, 1 1) gave 5 mg **5** (R_f 0 62)

Crude CC fraction 5 was also separated by MPC (60 g, SiO_2, see above) Fractions 1–8 (Et_2O) after addition of CH_2N_2 gave on TLC (Et_2O–petrol, 3 1) 20 mg methyl ester of hautriwaic acid (R_f 0 68) Fractions 9–15 (Et_2O–MeOH, 9 1) gave 180 mg 5-*O*-desmethylnobiletin (mp 143°, lit 144–146° [1], identified by ^{1}H NMR and MS) and fractions 16–25 (Et_2O–MeOH, 4 1) gave a crude fraction which showed in the ^{1}H NMR spectrum no acetate signal and was therefore acetylated in 10 ml $CHCl_3$ with 1 ml Ac_2O and 500 mg *p*-dimethylaminopyridine [10] TLC (Et_2O–petrol, 1 1) gave a crude acid which was purified further, after addition of CH_2N_2, by TLC (Et_2O–petrol, 1 3), affording 20 mg **9** (R_f 0 69) The purities of all the compounds were tested by TLC in different solvent mixtures and by 400 MHz ^{1}H NMR, where no impurities were visible

12α-[2-*Methylbutyryloxy*]-*hardwickiic acid methyl ester* (**2**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1725 (CO_2R, C=CCO_2R), 1645 (C=C), 875 (furan), MS *m/z* (rel int) 430 272 $[M]^+$ (0 1) (calc for $C_{26}H_{38}O_5$ 430 272), 399 $[M-OMe]^+$ (0 2), 381 $[399-H_2O]^+$ (0 1), 328 $[M-RCO_2H]^+$ (5 5), 313 $[328-Me]^+$ (7), 234 $[M-C_{11}H_{16}O_3]^+$ (52), 219 $[234-Me]^+$ (28), 203 $[234-OMe]^+$ (28), 175 $[203-CO]^+$ (14), 85 $[C_4H_9CO]^+$ (26), 57 $[85-CO]^+$ (100)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-113 \quad -119 \quad -138 \quad -266} \text{ (CHCl}_3\text{, } c \text{ 0 94)}$$

12α-*Hydroxyhautriwaic acid*-19-*lactone* (**4**). Colourless crystals, mp 133° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1775 (γ-lactone), 875 (furan), MS *m/z* (rel int) 330 183 $[M]^+$ (100) (calc for $C_{20}H_{26}O_4$ 330 183), 312 $[M-H_2O]^+$ (30), 282 $[312-CH_2O]^+$ (10), 219 $[M-C_6H_7O_2]^+$ (20), 218 $[M-C_6H_8O_2]^+$ (7), 204 $[219-Me]^+$ (41), 189 $[219-CH_2O]^+$ (30), 188 $[218-CH_2O]^+$ (45), 97 $[C_5H_5O_2]^+$ (50)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-115 \quad -121 \quad -139 \quad -260} \text{ (CHCl}_3\text{, } c \text{ 2 64)}$$

^{13}C NMR ($CDCl_3$, C-1–C-20) 20 5 *t*, 27 6 *t**, 143 5 *d*, 131 0 *s*, 45 7 *s*, 34 2 *t*, 27 9 *t**, 36 8 *d*, 39 2 *s*, 48 7 *d*, 44 6 *t*, 63 1 *d*, 138 4 *s*, 108 3 *d*, 138 3 *d*, 136 5 *d*, 17 6 *q*, 169 6 *s*, 71 9 *t*, 15 6 *q* (Signals labelled with an asterisk may be interchangeable)

20 mg **4** in 5 ml CH_2Cl_2 was stirred for 12 hr with 20 mg pyridinium dichromate TLC (Et_2O–petrol, 3 1) afforded 10 mg of the starting material (R_f 0 64) and 5 mg of the corresponding 12-oxo derivative (R_f 0 68), colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1780 (γ-lactone), 1680, 1670, 880 (β-furan ketone), MS *m/z* (rel int) 328 168 $[M]^+$ (19) (calc for $C_{20}H_{24}O_4$ 328 168), 284 $[M-CO_2]^+$ (3), 256 $[284-CO]^+$ (14), 219 $[M-CH_2COC_4H_3O]^+$ (100)

To 51 8 mg **4** (0 157 mmol) in 2 5 ml dry pyridine, 158 mg 2-phenyl butyric anhydride (0 505 mmol) was added After standing at room temp for 15 hr, H_2O and after 5 hr Et_2O and $NaHCO_3$ soln were added The organic phase was shaken twice with $NaHCO_3$ soln and the combined aq phases were acidified and the 2-phenyl butyric acid was extracted with Et_2O 130 mg 2-phenyl butyric acid was obtained, $[\alpha]_D$ −4 8° (C_6H_6, *c* 2 6) [optical yield 27% (−)]

The neutral phase gave after TLC (Et_2O–petrol, 1 1) 49 9 mg of the corresponding ester (R_f 0 63), colourless crystals, mp 164°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1765 (γ-lactone), 1725 (CO_2R), MS *m/z* (rel int) 476 256 $[M]^+$ (10) (calc for $C_{30}H_{36}O_5$ 476 256), 330 $[M-O=C=C(Ph)Et]^+$ (22), 312 $[M-RCO_2H]^+$ (24), 219 $[M-$side chain$]^+$ (34), 218 [McLafferty]$^+$ (41), 119 [ethyl tropylium]$^+$ (100), 94 [vinyl furan]$^+$ (97), 91 $[119-C_2H_4]^+$ (52)

7α,12α-*Dihydroxyhautriwaic acid*-19-*lactone* (**5**) Colourless crystals, mp 160°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 1755 (γ-lactone), 875 (furan), MS *m/z* (rel int) 346 170 $[M]^+$ (10) (calc for $C_{20}H_{26}O_5$ 346 170), 328 $[M-H_2O]^+$ (8), 316 $[M-CH_2O]^+$ (41), 298 $[316-H_2O]^+$ (5), 280 $[298-H_2O]^+$ (4), 204 (100), 176 $[204-CO]^+$ (48), 97 $[C_4H_3OCH{=}OH]^+$ (71)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-77 \quad -81 \quad -94 \quad -177} \text{ (CHCl}_3\text{, } c \text{ 0 11)}$$

12α-[2-*Methylbutyryloxy*]-*strictic acid methyl ester* (**6**-*methyl ester*) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3080, 1610 (C=CH_2), 1725 (CO_2R, C=CCO_2R), 880 (furan), MS *m/z* (rel int) 428 256 $[M]^+$ (3) (calc for $C_{26}H_{36}O_5$ 428 256), 396 $[M-MeOH]^+$ (1), 326 $[M-RCO_2H]^+$ (12), 232 $[M-$side chain$]^+$ (11), 201 $[232-OMe]^+$ (9), 173 $[201-CO]^+$ (28), 85 $[C_4H_9CO]^+$ (59), 57 $[85-CO]^+$ (100)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-151 \quad -162 \quad -186 \quad -334} \text{ (CHCl}_3\text{, } c \text{ 0 35)}$$

To 10 mg of the ester in 2 ml Et_2O, 20 mg $LiAlH_4$ was added After 15 min usual work-up afforded 6 mg **7**, colourless crystals, mp 164° (Et_2O), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3580 (OH), 875 (furan), MS *m/z* (rel int) 316 204 $[M]^+$ (14) (calc for $C_{20}H_{28}O_3$ 316 204), 298 $[M-H_2O]^+$ (7), 280 $[298-H_2O]^+$ (5), 267 $[298-CH_2OH]^+$ (5), 97 $[C_4H_3OCH{=}OH]^+$ (100)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-265 \quad -270 \quad -310 \quad -568} \text{ (CHCl}_3\text{, } c \text{ 0 08)}$$

1-*Acetoxy*-11-*carbomethoxy*-3,7,15-*trimethyl*-*hexa*-*deca*-2E,6E,10E,14-*tetraene* (**9**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1740, 1235 (OAc), 1715, 1640 (C=CCO_2R), MS *m/z* (rel int) 316 240 $[M-HOAc]^+$ (6 5) (calc for $C_{21}H_{32}O_2$ 316 240), 285 $[316-OMe]^+$ (2), 257 $[316-CO_2Me]^+$ (6), 135 $[CH_2C(Me){=}CHCH_2CH{=}C(Me)CH{=}CH_2]^+$ (21), 69 $[Me_2C{=}CHCH_2]^+$ (100)

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