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NEW HUMULENE DERIVATIVES FROM ASTERISCUS GRAVEOLENS

S. EL DAHMY, J. JAKUPOVIC, F. BOHLMANN* and T.M. SARG+

Institute of Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12; + Pharmacy College, Pharmacognosy Department, Zagazig University, Egypt

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Abstract – The aerial parts of Asteriscus graveolens afforded in addition to asteriscunolides A, B, C and D twelve further humulene derivatives, two bicyclic compounds also derived from humulene, a bisabolene derivative and the diisovalerate of coniferyl alcohol. The structures and the configurations of these compounds were determined mainly by spectroscopic methods. The problem of the proposed isolation of "stable conformers" of the asteriscunolides is discussed.

Introduction

So far not much is known on the chemistry of the small Mediterranean genus Asteriscus (= Odontospermum, tribe Inuleae, subtribe Inulinae). From the roots of three species trideca-pentaynene was isolated [1] while A. aquaticus L. contains unusual sesquiterpene lactones named asteriscunolide A - D and asteriscanolide [2,3].

We now have studied the aerial parts of Asteriscus graveolens Less., collected in Egypt, which also contain the asteriscunolides as well as the corresponding precursors 1a - 4a which also were isolated as their methyl esters 1 - 4 as well as the 6-acetoxy derivatives 5a - 8a which were isolated as their methyl esters 5 - 8.

For the structures of the asteriscunolides A - D pairs of conformers – A and C as well as B and D – were proposed. These pairs should differ only in the configuration of the $\Delta^{1(10)}$ double bond while the Δ^{7} double bond always should be E-configurated.

Though conformers of medium sized ring systems are well known, the isolation of conformers never has been reported previously. While one of the "conformers" could be transformed to the other (A → C) by heating at 200 °C (!) asteriscunolide B was stable even at 200 °C and could not be transformed to the "conformer" D. Accordingly, this structural assignment can not be accepted. The main reason for this assumption was the fact that the couplings of the Δ^{7} double bond were 13.5 Hz for asteriscunolide A and B and therefore an E-configuration was assumed. Detailed ^{1}H NMR studies including NOE and the use of shift reagents as well as ^{13}C NMR data have been carried out to establish this very unlikely assumption.

The ^{1}H NMR spectra of 1 - 8 (Table I) showed the same pattern. Again there were always pairs of compounds with $J_{7,8}$ = 13.5 and 17 Hz, respectively. The signals of all compounds could be assigned by spin decoupling. As the H-1 signals showed couplings with the olefinic methyl and two allylic

protons and as H-5 was coupled with allylic protons and with the proton under the acetate, respectively, these two signals were the starting points of the assignment. The configuration of the $\Delta^{1(10)}$ and Δ^{4} double bonds followed from the chemical shifts of H-1 and H-5, respectively, while the couplings of H-7 indicated the presence of an E- or Z-configurated Δ^{7} double bond. The ^{13}C NMR data (Table II) also supported these structures. The relatively large coupling (13.5 Hz) for the 7-Z-isomers obviously is due to the ring size [4] while an E-configuration, as proposed for two of the stable "conformers", was very unlikely. Broadening of several signals at room temperature already indicated the flexibility of these compounds. Partial reduction of 2 led to the alcohol 11. Its configuration also followed from the ^{1}H NMR data (Table I). Again in this compound $J_{7,8}$ was 13.5 Hz indicating that the conjugation was not reponsible for the magnitude of the coupling. UV irradiation transformed 6 to 8 and small amounts of 9 and 10 while irradiation of 7 gave mainly 8 and small amounts of 6, 9 and 10. Accordingly, the most stable isomers are 6 and 8 while those with a 7-E-double bond are much less stable. The configuration of the double bonds in 9 and 10 also followed from the ^{1}H NMR spectra (Table I). The strong down field shift of the H-5 signal obviously required a Z-configuration of the Δ^{4} double bond. This result clearly showed that 7 and 8 were the Δ^{7} E/Z-isomers and not conformers. Similary irradiation of asteriscunolide A gave a mixture containing mainly asteriscunolide A and B indicating that again the Δ^{7} E-isomers were less stable. In agreement with the configurations of 1 - 8 we therefore assign structures 12a - 12d for asteriscunolide A - D. The reported NOE data [2] are in agreement too with these configurations though a clear decision concerning the configuration of the Δ^{7} double bond can not be deduced from the data.

However, as an example, the NOE's observed with 6 indicated clearly a conformation with a Δ^{7} Z-configurated double bond. Irradiation of H-7 and H-8 gave clear NOE's with each other. Furthermore NOE's were present between H-12 and H-6 and H-7, between H-13 and H-6 and H-14, between H-7 and H-8, between H-14 and H-2α, between H-1 and H-5 and H-8 and between H-5, H-3β and H-1. This results lead to a conformation with C-14, C-15 and the keto group below and C-7 and C-8 above the plane, the 6-acetoxy group quasi equatorial and the keto group in plane with the $\Delta^{1(10)}$ double bond. The NOE's of 7 lead to a similar conformation, however, now the keto group is in plane with the Δ^{7} double bond. NOE's were present between H-6 and H-7, between H-14 and H-1 and H-6, between H-13 and H-6 and H-7, between H-12 and H-5 and H-8 and between H-1 and H-14, while no NOE was observed between H-7 and H-8.

The NOE's of 5 indicated that here again C-14 and C-15 are below the plane (NOE's between H-3β, H-5 and H-1, between H-12, H-8 and H-5, between H-13 and H-6 as well as between H-6 and H-7). Compound 8 showed clear NOE's between H-7 and H-8, between H-14 and H-1 and between H-5 and H-3.

In addition to the humulene derivatives 1 - 8 two minor cyclisized derivatives, the lactone 13 and the ester 14 were present as well as bisabolone (15), the 6-hydroxy derivative 16, coniferyl diisovalerate (17), chrysanthenol and its acetate and feruly aldehyde.

The structure of 13 followed from the molecular formula, the ^{1}H and the ^{13}C NMR data (s. Experimental), while the configuration could be deduced from the couplings and the NOE's. The double doublet at δ = 6.51 obviously was due to an olefinic proton in β-position to a keto group which showed an allylic coupling with a proton giving a threefold doublet at δ = 4.04 and a further small

coupling with that proton which displayed a narrowly split doublet at $\delta = 4.55$. As the IR spectrum indicated the presence of a γ-lactone (1780 cm^{-1}) these data led to a partial structure which only could be completed to 13 as spin decoupling allowed the assignment of the remaining sequence of H-1 - H-5. As H-1 showed an allylic coupling with the olefinic methyl group, the whole sequence was established as now the remaining carbons (C-11 - 13) only could be placed between C-7 and C-6. This required that the allylic proton H-5 was unusually shifted down field. However, in agreement with the molecular formula the ^{13}C NMR data indicated that an additional oxygen bearing carbon could be excluded. NOE's between H-13 and H-6, between H-4 and H-5 as well as between H-5 and H-6 led to the proposed stereochemistry which agrees with the most likely formation from 12a by proton catalyzed cyclization (s. Scheme). The ^{13}C NMR signals as well as the MS fragments nicely agreed with the proposed structure (s. Experimental). We have named lactone 13 1,10,7,8-tetra-dehydroasteriscanolide.

Compound 14, molecular formula $C_{16}H_{26}O_3$, showed IR bands for a non conjugated keto group (1710 cm^{-1}) and an ester group (1740 cm^{-1}) while the ^1H NMR spectrum (s. Experimental) indicated the absence of olefinic protons. Accordingly, a bicyclic systeme was likely. Spin decoupling allowed the assignment of all signals though those of H-1' and H-2 were overlapped multiplets. As H-5 only showed a small coupling with H-4 and $J_{1,10}$ were 11 and 4 Hz the proposed configuration was very likely. Surely also 14 was formed by proton catalyzed cyclization of the 1,10-dihydro derivative of 1 or its isomer. The corresponding 6,15-lactone has been reported from A. aquaticus [3].

The structure of 16 easily could be deduced from the ^1H and ^{13}C NMR data (s. Experimental) which were close to those of bisabolone (15) [5]. The presence of a hydroxy group at C-6 caused some shift differences in the ^1H NMR spectra of 15 and 16. Similar the structure of 17 easily could be deduced by comparing the ^1H NMR spectrum with those of corresponding coniferyl alcohol derivatives. The nature of the ester groups clearly followed from the typical ^1H NMR signals.

The presence of highly oxygenated humulene derivatives in two Asteriscus species may be of chemotaxonomic importance as these compounds are rare in the Compositae. So far only from Lychnophora species [6] humulene derivatives with several oxygen functions were isolated, while from a few other genera simple oxygenated compounds of this type are reported [7 - 12]. Only α-humulen-1(10)-epoxide [13] is more widespread. Investigations of biological activities of these new types of sesquiterpenes are in progress.

EXPERIMENTAL

IR spectra were recorded in CCl_4 on a Beckman IR 9 instrument, the NMR spectra on a Bruker WM 400 or WH 270 and EIMS were obtained at 70 eV with a Varian-MAT 711. TLC were performed on Si gel PF 254 and HPLC by using RP 8 columns, flow rate 3 ml/min. and 100 bar. Plant material (4.7 kg) was collected in July 1983 near Mamar Metla, Sinai desert, and extracted with 95% ethanol. After separation of the saturated long chain hydrocarbons by treatment of the extract with methanol 120 g extract was obtained. Column chromatography (CC) (Si gel) gave six fractions (starting with petrolether with raising amounts of Et_2O and finally Et_2O-MeOH, 4 : 1). Fraction 1 (Et_2O-petrolether, 1 : 10) gave 1.2 g chrysanthenyl acetate. Fraction 2 (5% of the total amount) (Et_2O-petrolether, 1 : 3) afforded by TLC (Et_2O-petrolether, 1 : 2) 14 mg 15 and 20 mg feruly l aldehyde. Fraction 3 (40% of the fraction) was separated again by medium

Table I. ^{1}H NMR spectral data of 1 - 11 (400 MHz, $CDCl_3$, TMS as internal standard)

	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-12	H-13	H-14	OAc	OMe
1$^+$ (57°)	5.85 br t			5.85 br t	2.42 m	6.18 d	6.00 d	1.19(6H) s		1.75 br s	-	3.74 s
2	6.47 br t					5.89 d	5.98 d	1.23(6H) br s		1.72 br s	-	3.71 s
2 (C_6D_6, 80°)	6.20 br t	2.32 m		5.57 t	2.50 m	5.27 d	5.88 d	0.89(6H) s		1.82 br s	-	3.40 s
3	5.90 br t			5.90 br t	2.46 m	5.36 d	5.94 d	1.13(6H) s		1.87 br s	-	3.72 s
3 (C_6D_6)	5.59 tq	2.32 m	2.24 m	5.67 t	2.66 d	5.84 d	5.23 d	1.08(6H) s		1.93 br s	-	3.45 s
4	5.38 m			5.81 m		6.68 d	5.96 d	1.23(6H) s		1.84 br s	-	3.78 s
4 (C_6D_6, 80°)	5.32 tq	2.31 m	2.03 m	5.52 t	2.53 m	6.70 d	5.92 d	0.99(6H) s		1.86 dt	-	3.55 s
5	5.72 br d	2.36 dddd 2.25 br d	2.99 br dd 2.16 ddd	6.06 d	5.60 d	6.30 d	6.12 d	1.04 s 1.13 s		1.67 br s	2.01 s	3.80 s
6	6.43 br d	2.69 dddd 2.32 br d	2.86 ddd 2.23 ddd	5.64 d	5.92 d	5.74 d	6.05 d	1.04 s 0.75 s		1.67 br s	2.07 s	3.70 s
7	5.34 br d	2.22 m 2.05 m	2.72 ddd 2.22 m	6.27 d	5.63 d	6.75 d	5.97 d	1.18 s 1.16 s		1.84 dd	2.05 s	3.69 s
8	5.90 br t	2.50 m	2.77 m 2.05 m	5.73 d	6.15 d	5.41 d	5.95 d	1.06 s 1.05 s		1.91 br s	2.12 s	3.77 s
9	6.26 br t	2.6 m	2.85 m 2.09 m	6.59 br d	5.53 d	6.11 d	5.58 d	1.25(6H) s		1.88 br s	2.03 s	3.73 s
10	6.24 br dd	2.65 br t 2.35 ddd	2.84 ddd 2.74 ddd	6.88 d	5.20 d	5.63 d	5.15 d	1.21 s 0.94 s		1.95 br s	2.00 s	3.79 s
11$^+$ ($CDCl_3$/ C_6D_6)	5.20 br t	2.25 m	2.50 ddd 2.10 m	5.44 dd	2.80 dd 2.10 dd	5.07 dd	5.43 dd	1.10 s 1.06 s		1.52 d	3.56 s	-

+) in C_6D_6 H-1 5.51 br t; H-5 5.44 t; +) 4.98 dd (H-9);

J [Hz]: Compound 1: 1,2 = 6.5; 5,6 = 9; 7,8 = 17; compound 2: 1,2 = 7; 5,6 = 9.5; 7,8 = 13.5; compound 3: 1,2 = 9; 1,14 = 1.5; 5,6 = 8; 7,8 = 13.5; compound 4: 1,2 = 8.5; 1,14 = 1; 5,6 = 9; 7,8 = 16.5; compound 5: 1,2 = 10; 2,2' = 13; 2,3 = 4; 2,3' = 12; 3,3' = 13; 5,6 = 11; 7,8 = 17; compound 6: 1,2 = 11.5; 1,2'~ 2; 1,14 ~1.5; 2,2' = 15; 2,3 = 5; 2,3' = 12; 2',3 = 2; 2',3' = 5; 3,3' = 12; 5,6 = 9; 7,8 = 13.5; compound 7: 1,2 = 12; 1,2'~ 3; 2,3 = 3,3' = 13; 2',3 = 4.5; 5,6 = 11; 7,8 = 16.5; compound 8: 1,2 = 9; 5,6 = 10; 7,8 = 13.5; compound 9: 1,2 = 8.5; 5,6 = 10.5; 7,8 = 13; compound 10: 1,2 = 12; 1,2' = 6; 2,2' = 13; 2,3 = 5; 2,3' = 2.5; 2',3 = 12; 2',3' = 5; 3,3' = 16; 5,6 = 11; 7,8 = 13.5; compound 11: 1,2 = 8; 2,3 = 4; 2,3' = 6; 3,3' = 12; 5,6 = 11; 5,6' = 7; 6,6' = 13; 7,8 = 13.5; 7,9 = 1.5; 8,9 = 7.

Table II. ^{13}C NMR spectral data of 2, 4 - 8 and 13 ($CDCl_3$, 100.6 Hz)

	2	4	5	6	7	8	13
C-1	150.4	129.4	146.8	150.2	128.7	139.3	129.7
C-2	25.4	31.2	25.1	25.5	31.6	31.4	30.8
C-3	34.6	33.4	35.1	34.5	32.5	32.4	23.9
C-4	139.1	138.8	139.0	139.3	139.3	138.4	47.9
C-5	142.8	141.6	136.3	142.7	138.6	138.6	45.2
C-6	41.7	40.3	75.5	78.5	73.8	75.8	87.7
C-7	143.9	160.9	155.8	138.6	156.7	137.8	150.9
C-8	128.2	126.9	128.5	129.5	127.6	130.5	135.0
C-9	201.0	203.0	203.3	200.5	203.1	200.3	198.7
C-10	129.8	132.8	135.7	129.9	134.3	132.7	138.4
C-11	40.6	37.3	40.9	43.3	40.9	44.0	49.1
C-12	25.4	29.7	18.2	22.1	20.9	21.6	26.7
C-13	29.7	29.7	26.4	27.3	26.6	21.6	20.7
C-14	11.0	21.1	12.1	11.0	18.4	21.0	22.6
C-15	167.0	168.4	167.0	166.6	167.5	167.5	176.9
OMe	51.0	51.3	51.9	51.4	51.7	51.7	-
$OCOCH_3$	-	-	170.2	169.8	170.2	170.2	-
	-	-	20.9	20.8	20.9	21.0	-

pressure chromatography (SiO_2, 30 - 60 μ, petrolether and raising amounts of Et_2O) which gave 700 mg 15, a mixture, which gave by TLC (EtOAc-C_6H_6, 1 : 9) 8 mg 17 and 140 mg of a mixture (3/2), 123 mg 16, a fraction which gave after repeated TLC (same solvent) 35 mg 1 and 73 mg of a mixture of 12a and 12b which could be separated by HPLC (MeOH-H_2O, 7 : 3). Fraction 3/2 was separated by HPLC (MeOH-H_2O, 7 : 3) affording 2.3 mg 3, 1.2 mg 14, 5 mg chrysanthenol, 45 mg 4 and 23 mg 2. The next CC fraction (13.1 g) contained following the ^1H NMR a complex mixture of acids and 12a - 12d. Therefore to 5 g in Et_2O CH_2N_2 was added and the mixture was separated by medium pressure chromatography (Si gel). With Et_2O-petrolether, 1 : 3, 170 mg ofa mixture of 1 - 4 were obtained followed by 120 mg 7, 82 mg 6, 65 mg 12a, then 81 mg of a mixture of 12b - 12d, a mixture of not esterified acids 1a - 4a which could not be separated, but after addition of CH_2N_2 1 - 4 could be seprated by TLC (EtOAc-C_6H_6, 1 : 9) and after TLC (Et_2O-petrol, 5 : 2) of the last fraction 2 mg 13. From the last CC fraction (14.3 g) 0.5 g was esterified with CH_2N_2 and separated by TLC (Et_2O-petrol, 5 : 2) affording two bands which after HPLC (MeOH-H_2O, 3 : 2) gave 1.2 mg 5 and 4.5 mg 8. The homogenity of all compounds was tested by TLC in different solvent mixtures and by their 400 MHz ^1H NMR spectra.

Methyl-9-oxo-1(10)Z,7Z-α-humulene-15-oate (3). Colourless oil; IR ν_{max} cm^{-1}: 1710 (CO_2R), 1650 (C=C-C=O); EIMS m/z 262.157 M^+ (6.5) ($C_{16}H_{22}O_3$), 247 M - Me (3), 230 M - MeOH (10), 150 (100), 135 (81), 96 (20).

Methyl-9-oxo-1(10)Z,7E-α-humulene-15-oate (4). Colourless oil; IR ν_{max} cm^{-1}: 1715 (CO_2R), 1660 (C=CC=O); EIMS m/z 262.157 M^+ (12) ($C_{16}H_{22}O_3$), 230 M - MeOH (6), 150 (100), 135 (71), 96 (70).

Methyl-6-acetoxy-9-oxo-1(10)E,7E-α-humu-

lene-15-oate (5). Colourless oil; EIMS m/z 320.162 M^+ (9) ($C_{18}H_{24}O_5$), 278 M - ketene (100), 261 M - OAc (3), 260 M - HOAc (4), 150 (57), 135 (17).

Methyl-6-acetoxy-9-oxo-1(10)E,7Z-α-humulene-15-oate (6). Colourless oil; IR ν_{max} cm^{-1}: 1740, 1250 (OAc), 1710 (CO_2R), 1660 (C=CC=O); EIMS m/z 320.162 M^+ (4) ($C_{18}H_{24}O_5$), 278 M - ketene (24), 260 M - HOAc (10), 150 (100), 135 (47), 96 (17).

Methyl-6-acetoxy-9-oxo-1(10)Z,7E-α-humulene-15-oate (7). Colourless oil; IR ν_{max} cm^{-1}: 1740, 1250 (OAc), 1715 (CO_2R), 1640 (C=CC=O); EIMS m/z 320.162 M^+ (2) ($C_{18}H_{24}O_5$), 150 (100), 135 (74), 96 (66).

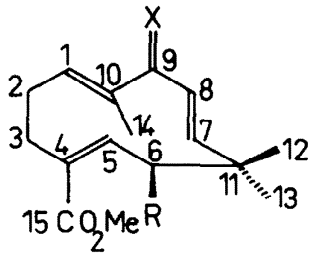
Methyl-6-acetoxy-9-oxo-1(10)Z,7Z-α-humulene-15-oate (8). Colourless oil; EIMS m/z 320.162 M^+ (6) ($C_{18}H_{24}O_5$), 278 M - ketene (31), 260 M - HOAc (10), 150 (100), 135 (52), 96 (34).

UV isomerization of 6, 7 and 12a.
The compounds in 20 ml petrolether were irradiated in the presence of 2 mg iodine for 2 h with UV light (mercury lamp). The mixtures obtained were separated by TLC (ether-petrolether, 2 : 1) A: 20 mg 6 afforded besides 8 mg 6, 8 mg 8, 1 mg 9, colourless oil; EIMS m/z 320.162 M^+ (9) ($C_{18}H_{24}O_5$), 278 M - ketene (19), 260 M - HOAc (16), 247 278 - OMe (10), 150 (100), 135 (56) and 1 mg 10, colourless oil; EIMS m/z 320.162 M^+ (7) ($C_{18}H_{24}O_5$), 278 M - ketene (27), 260 M - HOAc (17), 247 278 - OMe (7), 150 (100), 135 (53). B: 10 mg 7 gave 5 mg 8 and traces of 6, 7, 9 and 10. C: 10 mg 12a gave 4 mg 12a and 4 mg 12b.

1,10,7,8-Tetradehydro-asteriscanolide (13). Colourless crystals, mp. 172 °; IR ν_{max} cm^{-1}: 1780 (γ-lactone), 1665 (C=CCO); EIMS m/z 246.125 M^+ (70) ($C_{15}H_{18}O_3$), 231 M - Me (32), 201 M - HCO_2 (42), 200 M - HCO_2H (75), 174 M - $CH_2CH_2CO_2$ (100), 159 (86); $[\alpha]_D$ = + 30 ($CHCl_3$, c = 0.16); ^1H NMR ($CDCl_3$): 5.76 ddq (H-1), 2.21 m (H-2α), 2.63 br d (H-2β), 2.30 ddd (H-3α), 1.65 ddd (H-3β), 2.72 ddd (H-4), 4.04 ddd (H-5), 4.55 dd (H-6), 6.51 dd (H-7), 1.10 s (H-12), 1.23 s (H-13), 1.83 ddd (H-14); J [Hz]: 1,2α = 1,2β = 4; 1,14 = 2α,14 = 2β,14 = 1; 2α,2β = 20; 2α,3β = 3α,3β = 3β,4 = 12; 3α,4 = 2.5; 4,5 = 9; 5,6 = 5.5; 5,7 = 6,7 = 1.5; ^{13}C NMR ($CDCl_3$) (C-1 - C-15): 129.7, 30.8, 23.9, 45.2, 47.9, 87.7, 150.9, 135.0, 198.7, 138.4, 49.1, 26.7, 20.7, 22.6, 176.9.

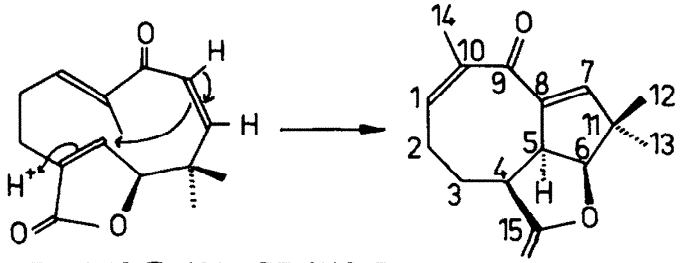
Methyl-3α,5α,8α,10αH-asteriscan-15-oate (14). Colourless oil; IR ν_{max} cm^{-1}: 1740 (CO_2R), 1710 (C=O); EIMS m/z 266.188 M^+ (2) ($C_{16}H_{26}O_3$), 234 M - MeOH (1), 206 M - HCO_2Me (2), 57 (100); ^1H NMR ($CDCl_3$): 1.69 m (H-1α), 1.65 m (H-1β), 1.5 m (H-2), 1.82 m (H-3α), 1.38 m (H-3β), 2.63 br d (H-4), 2.74 dddd (H-5), 1.64 dd (H-6α), 1.29 t (H-6β), 1.52 dd (H-7α), 1.42 tdd (H-7β) 3.25 ddd (H-8), 2.86 ddq (H-10), 1.08 s (H-12), 1.02 s (H-13), 1.01 d (H-14); J [Hz]: 1α,10 = 4; 1β,10 = 11; 3α,4 = 5; 3β,4 = 11; 4,5 = 3.5; 5,6α = 8; 5,6β = 5,8 = 6α,6β = 7α,7β = 12; 7α,8 = 7; 7β,8 = 12; 10,14 = 7.

6-Hydroxybisabol-2-en-1-one (16). Colourless oil; IR ν_{max} cm^{-1}: 3450 (OH hydrogen bonded), 1680, 1640 (C=CC=O); EIMS m/z 236.178 M^+ (0.6) ($C_{15}H_{24}O_2$), 219 M - OH (3), 218 M - H_2O (15), 203 218 - Me (3), 137 219 - C_6H_{10} (RDA) (69), 82 C_6H_{10} (RDA) (100), 69 C_5H_9 (41); ^1H NMR ($CDCl_3$): 5.80 br s (H-2), 2.35 and 2.25 m (H-4), 1.8 m (H-5), 1.70 tq (H-7), 1.30 m (H-8), 1.98 m (H-9), 4.93 tqq (H-10), 1.60 br s (H-12), 1.51 br s (H-13), 0.97 d (H-14), 1.91 br s (H-15); J [Hz]: 7,8 = 9,10 = 7,14 = 7; 10,12 = 10,13 = 1; ^{13}C NMR ($CDCl_3$) (C-1 - C-15): 202.9, 124.4, 162.3, 32.5, 30.1, 76.9, 35.1, 30.1, 26.0, 123.3, 131.4, 25.5, 17.6, 23.8, 13.2.



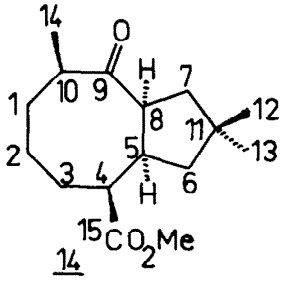
	1*	2	3	4	5	6	7	8	9	10	11
R	H	H	H	H	OAc	OAc	OAc	OAc	OAc	OAc	H
X	O	O	O	O	O	O	O	O	O	O	H OH
$\Delta^{1(10)}$	E	E	Z	Z	E	E	Z	Z	Z	E	E
Δ^{7}	E	Z	Z	E	E	Z	E	Z	Z	Z	Z
									(4E)	(4E)	

*) 1a–8a are the corresponding acids, numbering as in germacrane

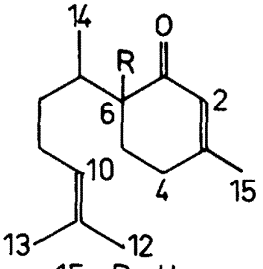


12a 7Z,1(10)Z 12b 7Z,1(10)E 13

12c 7E,1(10)E 12d 7E,1(10)E

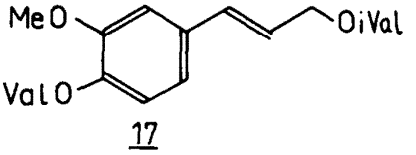


14



15 R=H

16 R=OH



17

Coniferyl-diisovalerate (17). Colourless oil; IR ν_{max} cm^{-1}: 1760 (PhOCOR), 1740 (CO_2R); EIMS m/z 348.194 M^+ (4) ($C_{20}H_{28}O_5$), 264 M - O=C=CHCHMe$_2$ (100), 180 264 - C_5H_8O (28), 163 264 - $^{\cdot}O_2CR$ (20), 85 $C_4H_9CO^+$ (44), 57 85 - CO (54); ^1H NMR ($CDCl_3$): 6.97 m (aromate), 6.60 br d (H-8), 6.21 dt (H-7), 4.72 dd (H-9), 3.83 s (OMe), 2.44 d, 2.28 tqq, 1.04 d (phenyl OIVal), 2.23 d, 2.13 tqq, 0.94 d (OIVal); J [Hz]: 7,8 = 16; 7,9 = 1; 8,9 = 6; 2',3' = 3',4' = 7.

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