SESQUITERPENOIDS FROM *Dittrichia viscosa* (L.) GREUTER. THEIR STRUCTURE AND DETERRENT ACTIVITY*

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In addition to the earlier described inuviscolide (*II*), the sesquiterpenic vachanic (*V*) and 2α--hydroxyisocostic (*VII*) acids, as well as carabron (*VIII*) and the so far undescribed sesquiterpenic lactone 11αH,13-dihydroconfertin were also isolated from *Dittrichia viscosa* (L.) GREUTER. For the last mentioned lactone the structure *IX* has been derived. The structure of vachanic acid (*V*) was confirmed by X-ray structural analysis. Compounds *V* to *VII* were tested for their deterrent (antifeedant) activity against selected insect pests living in corn stores, and they generally had a high activity.

In connection with our investigations of the components of the species of *Compositae* family and the study of their deterrent (antifeedant) activity we also investigated the species *Dittrichia viscosa* (L.) GREUTER (*Inulae* tribe, *Inulinae* subtribe). In the aerial parts of the mentioned species the sesquiterpenoids eudesma-3,11(13)-diene--12-carboxylic acid (*I*)[1,2], inuviscolide (*II*)[2], and deacetoxyxanthinin (*III*)[2] were already detected earlier. In the underground parts nine lactones structurally close to ineupatorolide B (*IV*) were detected in the group of sesquiterpenoids, of which two were obtained in pure state[3].

Now we isolated compound *V* from the aerial part of *D. viscosa*, identical with 4α-hydroxy-5αH,7αH,10βCH₃-eudesm-11(13)-ene-12-carboxylic acid (*V*) (synonym vachanic acid[4], illicic acid[5]). This sesquiterpenic acid has already been described in the species *Artemisia vachanica*[4], *A. serotina*[5], *Ambrosia illicifolia*[6], *A. camphorata*[7,8], *Hymenoclea salsola*[9], *H. monogyna*[10], *Fluorensia oolepsis*[11] and also in *Dittrichia graveolens*[12]. We added to the present knowledge concerning the pro-

perties of this acid its ^{13}C NMR data (Table I), which are in full agreement with the proposed structure *V*. We further prepared its methyl ester *VI* and also confirmed its structure by ^{1}H NMR and ^{13}C NMR data (Table I). In order to assign the signals we made use of the changes in chemical shifts of carbon atoms, elicited by *in situ* acylation of the hydroxyl at C(4) with trichloroacetyl isocyanate (TAI) in the NMR cell (for data see Table I).

We also confirmed the structure of 4α-hydroxy-5αH,7αH,10βCH₃-eudesm-11(13)--ene-12-carboxylic acid (*V*) by X-ray analysis. The final atomic parameters are collected in Tables II and III. The tables of the observed and the calculated structure amplitudes are available (U.R.) on request. The absolute configuration of the molecule cannot be independently determined on the basis of the present crystallographic experiment, but the positions in Tables II and III and the drawings were assigned on the assumption of the established configuration at C(7). The structural features are shown in Fig. 1 together with the atomic numbering and the thermal vibration ellipsoids for the non-hydrogen atoms scaled to 25% probability. The hydrogen

TABLE I

Carbon-13 chemical shifts of compounds *V—VIII* in deuteriochloroform

Carbon	V^a	VI^b	*VII*	*VIII*
C(1)	40·84	40·89 (−3·33)	48·34	22·91
C(2)	19·97	20·07 (−0·55)	66·78	23·33
C(3)	42·95	43·35 (−3·24)	124·46	43·58
C(4)	72·11	72·02 (18·61)	138·44	208·62
C(5)	54·66	54·69 (−3·23)	47·27	34·23
C(6)	26·94	27·26 (−0·08)	28·78	30·73
C(7)	40·00	40·37 (−0·41)	40·07	37·72
C(8)	26·67	26·41 (0·15)	26·55	75·57
C(9)	44·46	44·46 (0·09)	39·55	37·28
C(10)	34·56	34·55 (0·32)	35·51	17·22
C(11)	145·68	145·64 (−0·29)	144·88	128·95
C(12)	169·85	167·80 (−0·12)	172·05	c
C(13)	122·73	122·44 (0·24)	125·18	122·56
C(14)	18·63	18·66 (0·26)	20·89	18·23
C(15)	21·95	22·44 (−3·49)	16·25	20·09
OCH₃	—	51·72 (0·03)	—	—

^{a} Measured in the $C^2HCl_3 + C^2H_3O^2H$ (5 : 1) mixture; ^{b} the chemical shift changes induced by TAI-acylation of *V* are given in parentheses; ^{c} the signal was not detected probably due to very low intensity.

TABLE II

Final fractional coordinates and equivalent isotropic thermal parameters (A^2)

Atom	X	Y	Z	UEQ^a
C(1)	0·1636(5)	−0·1999(3)	−0·6195(2)	0·061(1)
C(2)	0·1486(6)	−0·1718(3)	−0·5308(2)	0·064(1)
C(3)	−0·0508(5)	−0·1471(3)	−0·5075(2)	0·057(1)
C(4)	−0·1836(5)	−0·2399(2)	−0·5270(2)	0·042(1)
C(5)	−0·1620(4)	−0·2740(2)	−0·6157(2)	0·0378(9)
C(6)	−0·2945(4)	−0·3650(2)	−0·6419(2)	0·0383(9)
C(7)	−0·3010(4)	−0·3713(2)	−0·7335(2)	0·0431(9)
C(8)	−0·1044(5)	−0·3898(3)	−0·7663(2)	0·058(1)
C(9)	0·0305(5)	−0·3021(3)	−0·7361(2)	0·060(1)
C(10)	0·0399(5)	−0·2966(3)	−0·6440(2)	0·047(1)
C(11)	−0·4320(5)	−0·4576(2)	−0·7660(2)	0·045(1)
C(12)	−0·5083(5)	−0·4412(3)	−0·8474(2)	0·050(1)
C(13)	−0·4806(7)	−0·5474(3)	−0·7285(2)	0·068(1)
C(14)	0·1253(6)	−0·4030(3)	−0·6114(2)	0·059(1)
C(15)	−0·1722(7)	−0·3340(3)	−0·4672(2)	0·056(1)
O(1)	−0·3722(3)	−0·1986(2)	−0·5172(1)	0·0488(8)
O(2)	−0·4924(4)	−0·3396(2)	−0·8741(1)	0·0612(9)
O(3)	−0·5836(5)	−0·5120(2)	−0·8858(2)	0·085(1)

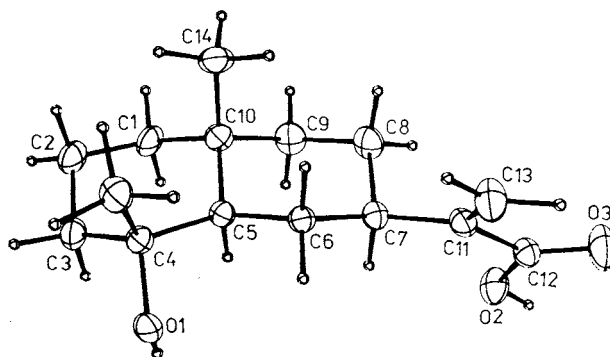^{a} $UEQ = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$.

FIG. 1

Perspective view of the molecule of vachanic acid (V). Non-H atom ellipsoids were drawn at 25% probability level[35]. H-atom spheres are on an arbitrary scale

atom spheres were drawn in an arbitrary scale. The conformation of the molecule is also described in terms of the torsion angles listed in Table IV.

The molecule of the acid *V* contains two *trans*-fused six-membered rings; an equatorial β-oriented α,β-unsaturated carboxylic group at C(7); two axial β-oriented methyl groups at C(10) and C(4) and a tertiary hydroxyl group at C(4) which is equatorial and α. Both cyclohexane rings have the chair conformation. The average torsion angle moduli are 53·1 (2·9)° and 58·1 (2·6)° for rings A and B, respectively, and may be compared with a value of 54·7° theoretically predicted for cyclohexane by Bixon and Lifson[13] and a value of 55·9 (4)° determined from electron diffraction studies of cyclohexane[14]. A slight flattening of the ring A at C(5), presumably introduced to minimize steric interactions of the axial methyl groups at C(10) and C(4), is followed by puckering of the B ring. Very likely the presence of two methyl groups is also responsible for the lengthening of the C(4)—C(5) and C(5)—C(10) bonds

TABLE III
Final H-atom fractional coordinates (.10^3) and isotropic temperature factors (.10^3)

Atom	X	Y	Z	U
H(11)	123	−129	−654	68
H(12)	306	−220	−633	68
H(21)	233	−101	−518	68
H(22)	198	−241	−496	68
H(31)	−95	−75	−539	68
H(32)	−56	−132	−444	68
H(51)	−203	−200	−647	68
H(61)	−247	−442	−618	68
H(62)	−432	−348	−619	68
H(71)	−356	−294	−754	68
H(81)	−109	−387	−831	68
H(82)	−56	−469	−747	68
H(91)	167	−320	−759	68
H(92)	−14	−223	−758	68
H(131)	−566	−603	−755	68
H(132)	−439	−562	−674	68
H(141)	36	−471	−626	84
H(142)	147	−400	−548	84
H(143)	257	−414	−641	84
H(151)	−32	−365	−466	84
H(152)	−265	−399	−485	84
H(153)	−209	−305	−408	84
HO(1)	−385	−139	−549	68
HO(2)	−543	−326	−923	68

which are the longest in the structure $\left(1\cdot551(4) \text{ and } 1\cdot557(5) \text{ Å}*\text{, respectively}\right)$, and for the widening of the bond angle C(4)—C(5)—C(10) to a value of $115\cdot7(2)°$. The remaining bond distances and angles are within the normal ranges. The conformation of the carboxyl group in the crystal is such that the C=C—C=O group has the synplanar arrangement, commonly observed in carboxylic acids[15]. The projection of the structure along the x axis, demonstrated in Fig. 2, shows the hydrogen bonding pattern in the crystal lattice. The H-bonded molecules form a three-dimensional network which plays an essential role in packing. The tertiary hydroxyl group acts both as a donor (to carbonyl oxygen) and an acceptor (hydrogen from the carboxyl group) of proton. Table V gives relevant bond distances and angles.

The further substance isolated by us, *VII*, had m.p. 153—156°C, $[\alpha]_D^{20}$ +48·4° and the composition $C_{15}H_{22}O_3$. According to a comparison of ^1H NMR spectra it is identical with 2α-hydroxyisocostic acid (*VIII*) which was isolated from the species *Schistostepium crataegifolium* (DC) FENZL. ex HARV.[16]. We completed its characterization by ^{13}C NMR data (Table I) and CD spectrum, even though it was described earlier[16] as a gum with a lower $[\alpha]_D$ value.

We further isolated carabron (*VIII*) which was isolated up to now from *Carpesium abrotanoides*[17], *C. eximium*[18], *Helenium quadridentatum*[19], *Arnica foliosa*[20], *A. longifolia*[21], *Inula helenium*[22], and *I. toyleana*[22]. The ^{13}C NMR data of compound *VIII* are in Table I.
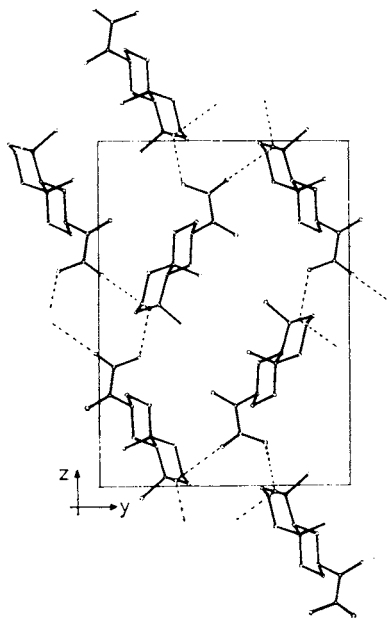

z ↑
└——→ y

FIG. 2

The molecular packing in the crystal viewed along the x axis. For details of hydrogen bonds (broken lines) see Table V

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* $1 \text{ Å} = 10^{-10}$ m.

TABLE IV

Torsion angles (deg) with estimated standard deviations in parentheses

Atoms	Angle	Atoms	Angle
C(10)—C(1)—C(2)—C(3)	−56·8(4)	C(6)—C(5)—C(10)—C(1)	177·2(3)
C(2)—C(1)—C(10)—C(5)	52·6(3)	C(6)—C(5)—C(10)—C(9)	60·2(3)
C(2)—C(1)—C(10)—C(9)	167·4(3)	C(6)—C(5)—C(10)—C(14)	−60·7(3)
C(2)—C(1)—C(10)—C(14)	−73·1(3)	C(5)—C(6)—C(7)—C(8)	56·9(3)
C(1)—C(2)—C(3)—C(4)	56·5(3)	C(5)—C(6)—C(7)—C(11)	−178·7(3)
C(2)—C(3)—C(4)—C(5)	−52·2(3)	C(6)—C(7)—C(8)—C(9)	−54·7(3)
C(2)—C(3)—C(4)—C(15)	77·5(4)	C(6)—C(7)—C(11)—C(12)	154·9(3)
C(2)—C(3)—C(4)—O(1)	−168·7(3)	C(6)—C(7)—C(11)—C(13)	−26·8(4)
C(3)—C(4)—C(5)—C(6)	−178·3(3)	C(11)—C(7)—C(8)—C(9)	178·7(3)
C(3)—C(4)—C(5)—C(10)	50·3(3)	C(8)—C(7)—C(11)—C(12)	−81·1(3)
C(15)—C(4)—C(5)—C(6)	53·3(3)	C(8)—C(7)—C(11)—C(13)	97·2(4)
C(15)—C(4)—C(5)—C(10)	−78·2(3)	C(7)—C(8)—C(9)—C(10)	57·3(3)
O(1)—C(4)—C(5)—C(6)	−61·3(3)	C(8)—C(9)—C(10)—C(1)	−174·7(4)
O(1)—C(4)—C(5)—C(10)	167·2(3)	C(8)—C(9)—C(10)—C(5)	−57·6(3)
C(4)—C(5)—C(6)—C(7)	164·6(3)	C(8)—C(9)—C(10)—C(14)	66·4(4)
C(4)—C(5)—C(10)—C(1)	−50·2(3)	C(7)—C(11)—C(12)—O(2)	−17·1(3)
C(4)—C(5)—C(10)—C(9)	−167·3(3)	C(7)—C(11)—C(12)—O(3)	165·1(4)
C(4)—C(5)—C(10)—C(14)	71·9(3)	C(13)—C(11)—C(12)—O(2)	164·5(4)
C(10)—C(5)—C(6)—C(7)	−62·0(3)	C(13)—C(11)—C(12)—O(3)	−13·3(4)

TABLE V

Distances (Å)[a] and angles (deg) in the hydrogen bonding system

Acceptor position D—H ⋯ A	D—H	H ⋯ A	D ⋯ A	Angle D—H ⋯ A
O(1)—H(01)⋯O(3) −1 − x, 1/2 + y, −3/2 − z	0·90(4)	1·91(4)	2·814(4)	178(3)
O(2)—H(02)⋯O(1) −1 − x, −1/2 − y, −1/2 + z	0·91(4)	1·71(4)	2·629(3)	177(3)

[a] 1 Å = 10^{-10} m.

We further obtained the already described (in this species) non-crystalline inu-viscolide (*II*), the identity of which we demonstrated by comparison of its ^{1}H NMR data with those published earlier[2].

I

II

III

IV

V, R = H
VI, R = CH$_3$

VII

VIII

IX
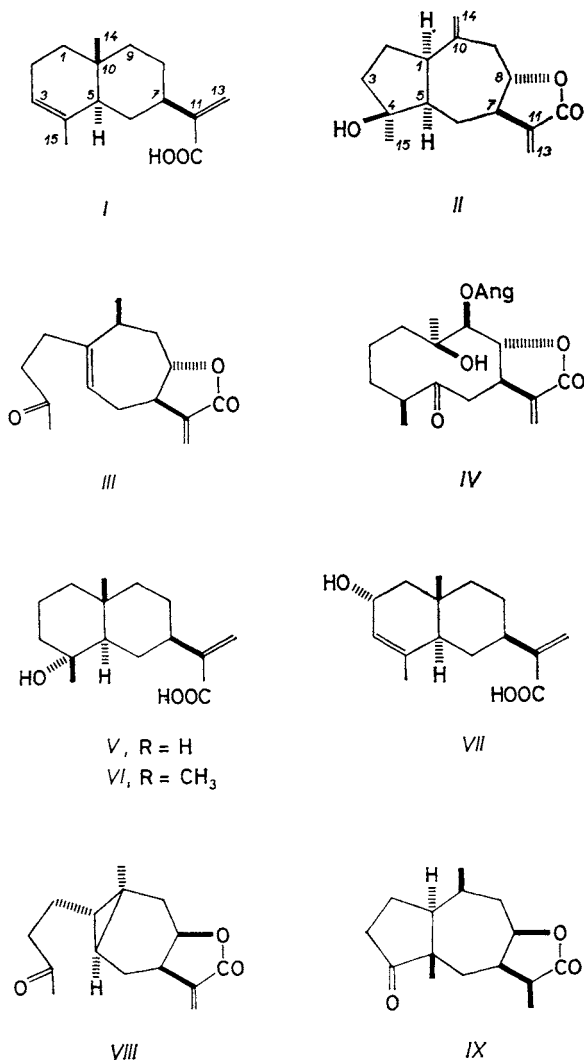
The investigated plant material also afforded compound *IX*, m.p. 138−140°C and composition $C_{15}H_{22}O_3$, which according to its spectrum contains a γ-lactone ring ($1\,770\,cm^{-1}$) and an oxo group on a five-membered ring ($1\,738\,cm^{-1}$). The mass spectrum contained a molecular peak at m/z 250 and its CD spectrum displayed a Cotton effect at 296 nm with Δε +2·6 and 217 nm with Δε +1·2. The ^{1}H NMR

spectrum proved the presence of one tertiary methyl group $(\delta\ 1\cdot04\ \text{s})$ and two secondary methyl groups $(\delta\ 1\cdot10\ \text{d}, J = 6\cdot8\ \text{Hz and}\ \delta\ 1\cdot19\ \text{d}, J = 7\cdot4\ \text{Hz})$, a multiplet of a —CH—O hydrogen in position 8 $(\delta\ 4\cdot64\ \text{ddd}, J = 11\cdot5;\ 6\cdot4,\ \text{and}\ 4\cdot3\ \text{Hz})$ and the hydrogen H(11) $(\delta\ 2\cdot87\ \text{dq}, J = 9\cdot3;\ 7\cdot4\ (3\times))$. The remaining 13 hydrogens resonate in the $\delta\ 1\cdot6-2\cdot6$ region and the extraction of their NMR parameters is very difficult. The identified signals led to the structure of 11αH,13-dihydroconfertin (IX). We derived the absolute configuration of this compound from the CD spectrum which is similar to the CD spectrum of tetrahydrohelenalin $(X;\ 294\ \text{nm},\ \Delta\varepsilon\ +0\cdot7;\ 215\ \text{nm},$ $\Delta\varepsilon\ +0\cdot8)$. This fact indicates that the absolute configuration at C(1) and C(5) (according to the Cotton effect at 296 nm in lactone IX) and the absolute configuration at C(11) (according to the Cotton effect at 217 nm) is analogous to the absolute configuration of tetrahydrohelenalin and that, therefore, formula IX also expresses the absolute configuration. Compound IX is very probably identical with dihydro-anhydrocumanin, prepared from cumanin[23]. A detailed comparison was impossible because in paper[23] the NMR data for compound IX are not given. As a native compound 11αH,13-dihydroconfertin (IX) was detected in the plant species investigated for the first time.

The tests of the deterrent antifeedant activity were carried out, using the described method[24,25], with both sesquiterpenic acids V and VII, with methyl ester VI, and helenalin (XI) as standard. These substances were tested on adult specimens of the

TABLE VI
The deterrent activity of compounds $V—VII$

Compound	Coefficients					
	relative	absolute	total	relative	absolute	total
	Adults of *Sitophilus granarius*			Adults of *Tribolium confusum*		
V	73·5	41·6	115·1	54·2	44·8	99·0
VI	91·0	67·5	158·5	100·0	37·7	137·7
VII	96·9	54·2	151·1	100·0	38·2	138·2
X	100·0	100·0	200·0	100·0	43·3	143·3
	Larvae of *Trogoderma granarium*			Larvae of *Tribolium confusum*		
V	13·3	5·5	18·8	100·0	60·3	160·3
VI	47·2	14·3	61·5	92·6	70·0	162·6
VII	39·0	30·5	69·5	83·4	60·5	143·9
X	98·3	74·0	172·3	100·0	85·8	185·8

species *Sitophilus granarius* L. and *Tribolium confusum* Duv. and on the larvae of the last mentioned species and the species *Trogoderma granarium* Ev. The results are summarized in Table VI. A very high deterrent activity (the value of "total coefficients" in Table VI between 150 and 200)[24,26] against adults of *S. granarius* was found in acid *VII* and methyl ester *VI*, and against larvae of *Tribolium confusum* in acid *V* and its methyl ester *VI*. Compounds *VI* and *VII* displayed a medium activity (the value of "total coefficients" in Table VI between 100 — 150)[24,26] against adults of *Tribolium confusum*. The larvae of *Trogoderma granarium* were relatively least affected by the substances tested. It further followed from the experiments that acid *VII* has an averagely higher deterrent activity in comparison with acid *V* and that methyl ester *VI* also has an averagely higher deterrent activity in comparison with the free acid *V*. All these substances, displaying a strong anti-feedant activity contain an exomethylene double bond conjugated with the free or the bound carboxyl function in the molecule.

X XI
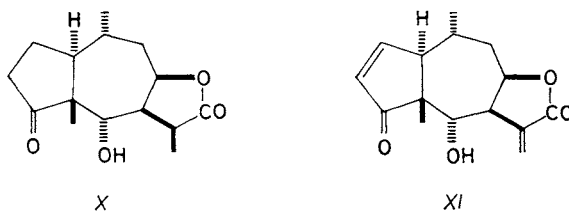
The species *Dittrichia viscosa* (L.) Greuter (synonym *Inula viscosa* (L.) Ait.), together with the species *D. graveolens* (L.) Greuter (synonym *I. graveolens* (L.) Desf.), are the only species of the *Dittrichia* Greuter genus[27]. This genus belongs together with other genera to the group *Inula* which together with the groups *Carpesium* and *Geigeria* constitute the subtribe *Inulinae*[28]. The common component of both species of the *Dittrichia* genus is so far only vachanic acid (*V*) which was isolated, of course, as already mentioned, from a number of species belonging to various tribes of the *Compositae* family, and hence it cannot be considered a character of the *Dittrichia* genus. Graveolide (*XII*), which was described as a component of *D. graveolens*[29], has not yet been detected in *D. viscosa*, while on the other hand the components of sesquiterpenic character detected in this species have not been identified in *D. graveolens*. Therefore it seems problematic whether the sesquiter-penoid components will be able to represent a criterion for the systematics of the mentioned taxon in this case.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Silica gel for column chromatography was prepared according to Pitra and Štěrba (30 — 60 mμ, deactivated

by addition of 11% of water). Thin-layer chromatography was carried out on silica gel G (Merck) according to Stahl. The IR spectra were measured in chloroform, unless stated otherwise, on a Perkin–Elmer PE 580 spectrophotometer. The ^{1}H and ^{13}C NMR spectra (200 MHz or 50·3 MHz, respectively) were measured on a Varian XL 200 instrument in deuteriochloroform, using tetramethylsilane as internal reference. Chemical shifts and the coupling constants of protons were obtained by first order analysis from the expanded spectrum (2 Hz/cm) using exponential multiplication with gaussian apodization function for resolution enhancement. The mass spectra were measured on an AEI MS 902 spectrometer, optical rotation was determined in methanol on an objective polarimeter Perkin–Elmer 141. The CD spectra were measured on a Roussel–Jouan CD 185 dichrographe.

Isolation of Sesquiterpenoids

The fresh aerial part of *Dittrichia viscosa* (L.) GREUTER species (12 kg) was collected in August, 1983 (voucher RL 549/83 is deposited in the herbarium of Zaklad Roślin Leczniczych, Akademia Medyczna, Poznań, Poland), and worked up as described earlier[30]. The chloroform extract obtained (35 g) was dried over anhydrous sodium sulfate and concentrated. On cooling a mixture of vachanic (*V*) and 2α-hydroxyisocostic acid (*VII*; 5·0 g; m.p. 158—160°C) crystallized out. Re-chromatography of the mixture of both acids (600 mg) on a silica gel column (80 g) with benzene containing 20% of acetone gave acid *V* in early fractions, m.p. 174—176°C (diisopropyl ether) and $[\alpha]_D^{20}$ −45·6° (*c* 0·4). Mass spectrum (*m/z*): 252 (M), 237, 234 (M − 18), 219, 206 (M − COOH), 191, 177, 164, 149, 121, 108, 81, 71, 43. IR spectrum (cm⁻¹): 1 692, 3 000 (carboxyl), 1 623 (double bond). CD spectrum (nm, Δε): 250, +0·1; 235, ±0; 215, − 1·8 (last reading). From further fractions acid *VII* was isolated, m.p. 153—156°C (benzene) and $[\alpha]_D^{20}$ +48·4° (*c* 0·4) and composition $C_{15}H_{22}O_3$. Mass spectrum (*m/z*): 250 (M), 232 (M − 18), 217, 199, 171, 143, 110. IR spectrum (cm⁻¹): 3 365 (hydroxyl), 1 690 (carbonyl), 1 630 (double bond). CD (nm, Δε): 213, +4·1. For $C_{15}H_{22}O_3$ (250·3) calculated: 71·97% C, 8·86% H, 0·81% H act.; found: 72·16% C, 8·97% H, 0·92% H act. From the mother liquors after crystallization of both acids (15·3 g) and chromatography on silica gel (300 g) with toluene with addition of chloroform and HPLC (using 8 × 300 mm column; Lichrosorb Si-60 10 μm; hexane–30% ethylacetate) carabron (*VIII*) with m.p. 89—90°C and $[\alpha]_D^{20}$ +46·3° was obtained in the early fractions in addition to another fraction of both acids *V* and *VII*. The IR and ^{1}H NMR spectra were identical with similar spectra of a standard sample[20]. A mixture with a reference sample[20] melted without depression. From further fractions rechromatography by HPLC in hexane–30% ethylacetate gave 11αH,13-dihydroconfertin (*IX*), m.p. 138—140°C. IR spectrum (cm⁻¹): 1 770 (γ-lactone), 1 738 (five-membered cyclic ketone). Mass spectrum (*m/z*): 250 (M), 232 (M − 18), 177, 159, 133, 119, 107. CD spectrum (nm, Δε): 296, +2·6; 245, ±0; 217, +1·2. For $C_{15}H_{22}O_3$ (250·3) calculated: 71·97% C, 8·86% H; found: 71·77% C, 9·02% H. From later fractions (500 mg) noncrystalline inuviscolide (*II*; 120 mg) was obtained by HPLC in hexane–30% ethylacetate the IR and ^{1}H NMR spectra of which were identical with similar spectra described in literature[2].

Methyl Ester of Vachanic Acid (*VI*)

An excess of ethereal diazomethane solution was added to a solution of acid *V* (200 mg; 0·79 mmol) in 10 ml of methanol and the mixture was allowed to stand at room temperature for 5 min. The solution was evaporated and the residue gave methyl ester *VI* (200 mg) with m.p. 55—56°C, $[\alpha]_D^{20}$ −36·9° (*c* 0·3) and composition $C_{16}H_{26}O_3$. Mass spectrum (*m/z*): 266 (M), 248 (M − 18), 232, 223, 206, 191, 181, 149, 121. IR spectrum (cm⁻¹): 3 540, 3 250 (hydroxyl), 1 717 (α,β-unsaturated ester), 1 622 (double bond). CD spectrum (nm, Δε): 250, +0·2; 233, ±0; 215, −1·4.

For $C_{16}H_{26}O_3$ (266·4) calculated: 72·14% C, 9·84% H, 0·76% H act.; found: 72·07% C, 9·93% H, 0·88% H act..

X-Ray Structure Determination

X-Ray diffraction data were collected on a Syntex $P2_1$ diffractometer from a crystal of 0·5 × × 0·5 × 0·5 mm dimensions. The crystals are orthorhombic, $P22_12_1$, with $a = 7·2175(7)$, $b = = 12·197(2)$, $c = 16·475(2)$ Å, $V = 1\ 474·2(4)$ Å^3, $D_x = 1·13$ g cm^{-3} for $Z = 4$, Mo K$\alpha, \lambda = = 0·71093$ Å, $\mu = 0·044$ mm^{-1}. 1 440 reflections were measured in one octant of which 1 102 had $I \geqq 1·96\sigma$ (I) and were considered observed. The background and integrated intensity for each reflection were evaluated from profile analysis according to the Lehman and Larsen method[31], using PRARA program[32]. Lorentz and polarization corrections were applied to the structure factors but no absorption corrections were made.

The structure was solved with MULTAN[33]. The positions of most of the hydrogen atoms were calculated geometrically, but methylene hydrogen atoms as well as the hydroxyl hydrogen atoms were located on a difference Fourier map and their positional parameters were allowed to refine freely. The molecular model was refined by full-matrix least-squares technique with non-H atoms anisotropic. Methyl hydrogen atoms were refined as a rigid group with a common temperature factor which converged to a value of $U = 0·084(5)$ Å^2. The remaining H-atoms were refined using a "riding model"; the common isotropic temperature factor for non-methyl hydrogen atoms converged at $U = 0·063(3)$ Å^2. In the final stages of the refinement an empirical isotropic extinction parameter x was introduced to correct the calculated structure factors by multiplying by $1 - xF_c^2/\sin \Theta$ and it refined to a value $1·8(1) . 10^{-6}$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1·4900/(\sigma^2(F_o) + 0·0025F_o^2)$. The final R value was 0·038 and $wR = 0·059$ for 1 102 reflections and 184 parameters. The refinement was carried out using SHELX-76 program[34], the molecular geometry was studied using programs included in CRYPOZ library[32] and ORTEP[35] was used to prepare drawings.

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Note added in proof: In formulae *V* and *VI* ROOC should be placed instead of HOOC.