41291-42-3; $(CH_2)_3(NCMe_3)_2PH$, 55342-78-4; $(CH_2)_2(NCMe_3)_2PH$, 89437-95-6; $(i\text{-}Pr_2N)(MeO)PH$, 89437-96-7; $(MeO)_2PH$, 20502-63-0; $(i\text{-}Pr_2N)(EtO)PH$, 89437-97-8; $(i\text{-}Pr_2N)(i\text{-}PrO)PH$, 89437-98-9; $(i\text{-}PrO)_2PH$, 88542-86-3; $(i\text{-}Pr_2N)(Me_3CO)PH$, 89437-99-0; $(Me_3CO)_2PH$, 2171-76-8; $(Me_3CO)_2P(O)H$, 13086-84-5; $(Et_2N)(EtO)PH$, 89438-00-6; $(EtO)_2PH$, 20502-85-6; $(Et_2N)(Me_3CO)PH$, 89438-01-7; $(Et_2N)_2PCH{=}CH_2$, 89438-02-8; $(CH_2)_3(NCMe_3)_2PCH{=}CH_2$, 89438-03-9; $(i\text{-}Pr_2N)_2PCH{=}CH_2$, 89438-04-0; $(Et_2N)_2PCH_2CH_2P(NEt_2)_2$, 86926-28-5; $(CH_2)_3(NCMe_3)_2PCH_2CH_2P(NCMe_3)_2(CH_2)_3$, 89438-05-1; PCl_3, 7719-12-2; $i\text{-}Pr_2NH$, 108-18-9; Et_2NH, 109-89-7; $(CH_2)_3(NHCMe_3)_2$, 22687-38-3; $(CH_2)_2(NHCMe_3)_2$, 4062-60-6; MeOH, 67-56-1; EtOH, 64-17-5; i-PrOH, 67-63-0; Me_3COH, 75-65-0; $(Me_2N)_3P$, 1008-26-0; $LiAlH_4$, 16853-85-3; $CH_2{=}CHBr$, 593-60-2.

Correct Structures of Montanin C, Teupolin I, and 12-*epi*-Teucvin, Three (12*R*)-Neoclerodan-20,12-olides Isolated from the *Teucrium* Species

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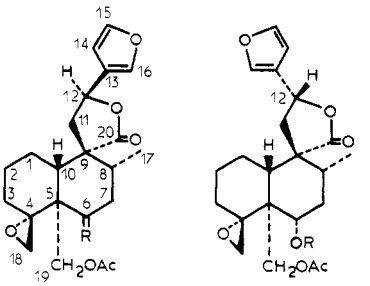
The previously assigned C-12(*S*) configuration for teupolin I (**2**) and montanin C (**3**) must be amended to C-12(*R*) (**4** and **5**, respectively) as the result of extensive ^1H and ^{13}C NMR spectroscopic studies, chemical correlations, and an X-ray diffraction analysis of montanin C which provided only its relative configuration. In addition, the structure of a new diterpenoid, 12-*epi*-teucvin (**7**), which also possesses a C-12(*R*) stereochemistry, has been ascertained. Comparative studies between three pairs of C-12 epimers allowed us to establish some criteria for determining the stereochemistry at C-12 of neoclerodan-20,12-olide derivatives by means of ^1H and ^{13}C NMR spectroscopy. In particular, the compounds with a C-12(*R*) configuration showed a clear NOE between the C-17 and the C-12 protons, which was not observed in the epimers belonging to the C-12(*S*) series.

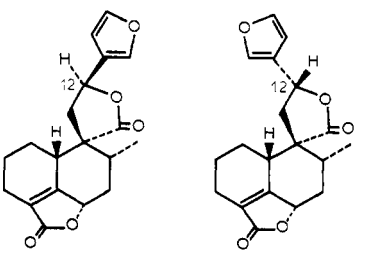
A large number of diterpenoids with the clerodane skeleton have been isolated from plants in the last few years.[2] Interest in these compounds has been stimulated by their biological activity as insect antifeedants and as antitumor, antimicrobial, and antifungal agents.[3] The *Teucrium* species (family Labiatae) have afforded a number of neoclerodane and 19-norneoclerodane diterpenoids,[4] some with unusual and fascinating structures.[4d-f]

Two years ago[5] we established the structure of the diterpenoid 19-acetylgnaphalin (**1**, Chart I) by means of an X-ray diffraction analysis, and we pointed out that the sodium borohydride reduction of **1** yielded a compound (**2**) which could, in principle, be identical with teupolin I, a diterpenoid previously isolated from *Teucrium polium*,[6] although some of their physical data did not entirely agree. At the same time we pointed out that the acetyl derivative

Chart I



1 R = O
2 R = αOH, βH
3 R = αOAc, βH
4 R = H
5 R = Ac



6 **7**

3 had physical and spectral data which differed from those reported[7] for montanin C, another diterpenoid found in *Teucrium montanum*, to which structure **3** had been repeatedly attributed.[6-8] Shortly afterwards, Miyase and

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0022-3263/84/1949-1789$01.50/0

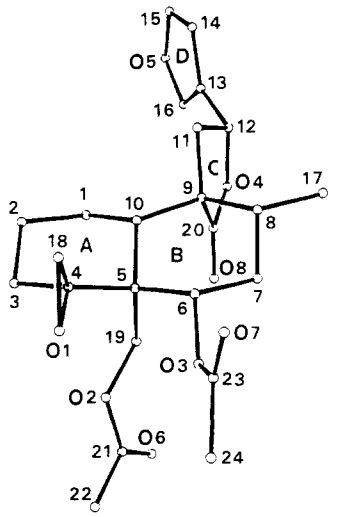

Figure 1. X-ray molecular model of one (**5b**) of the two crystallographically independent molecules of montanin C (**5**).

co-workers[9] isolated from the aerial part of *Teucrium japonicum* a diterpenoid, teucjaponin B, whose structure was rigorously proved, by chemical correlation with 19-acetylgnaphalin (**1**), to be identical with **2**, but whose physical and spectroscopic data did not agree, either, with those reported for teupolin I.[6] In view of these facts, it was obvious that some aspects of the reported structures of teupolin I[6] and montanin C[7] needed to be reexamined.

We have recently isolated from *Teucrium scorodonia*[10] and from *Teucrium lanigerum*[11] a diterpenoid with identical physical data to those reported for teupolin I,[6] and we have also found[12] montanin C[7,8] among the diterpenic constituents of *Teucrium massiliense*. At this point, having in our hands authentic samples of compounds **2**, **3**, teupolin I, and montanin C, we have undertaken a detailed study in order to establish the correct structures of the latter two compounds. On the basis of the data reported here, we definitely conclude that teupolin I and montanin C are correctly represented by the formulae **4** and **5**, respectively, and not by the formulae **2** and **3**, respectively, as has been previously proposed.[6-8]

Between compounds **2**[5] (teucjaponin B)[9] and **4** (teupolin I),[6] and similarly between compounds **3**[5] and **5** (montanin C),[7] there were noticeable differences in their physical data (Table I) and marked differences in their ^{13}C NMR spectra (Table II), but striking similarities in their ^{1}H NMR spectra (Table III) and almost identical IR, UV, and mass spectra.[5-7,9]

Acetic anhydride–pyridine treatment of teupolin I (**4**) isolated from *Teucrium scorodonia*[10] and from *Teucrium lanigerum*[11] (identical with the product isolated from *Teucrium polium*[6]) yielded montanin C (**5**, identical with the diterpenoid isolated from *Teucrium montanum*[7] and from *Teucrium massiliense*[12]), thus establishing that teupolin I is the 6-deacetyl derivative of montanin C.

Table I. Comparison of Physical Data of Compounds 2-7

	2	3	4	5	6	7
molecular formula	$C_{22}H_{28}O_7$	$C_{24}H_{30}O_8$	$C_{22}H_{28}O_7$	$C_{24}H_{30}O_8$	$C_{19}H_{20}O_5$	$C_{19}H_{20}O_5$
mp, °C (solvent)	256-259 (EtOAc-*n*-hexane);[5] 255-258 ($CHCl_3$–MeOH)[9]	163-164 (Et_2O-*n*-hexane)[5]	211-213 ($CHCl_3$–Et_2O);[6] 217-220 (MeOH)[10,11]	182-183 (EtOAc–Et_2O);[7] 184-186 (MeOH)[12]	207-208 (MeOH)[15b]	197-199 (EtOAc-*n*-hexane)
$[\alpha]_D$, deg ($CHCl_3$)	+68.1 (*c* 0.43);[5] +45.5 (*c* 0.67)[9]	+33.5 (*c* 0.97)[5]	+60 (*c* 2);[6] +59.1, (0.62)[10,11]	+8.4 (*c* 0.262);[7] +7.4 (*c* 0.891)[12]	+184 (*c* 0.12)[15b]	+222.6 (*c* 0.694)

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Table II. ^{13}C Chemical Shifts of Compounds 2-7[a]

	2[b]	4[b]	Δδ[c]	3	5	Δδ[c]	6[d]	7	Δδ[c]
C(1)	22.6 t[e]	22.0 t	-0.6	22.9 t	22.2 t	-0.7	21.6 t	21.9 t	+0.3
C(2)	25.0 t	24.9 t	-0.1	24.9 t	24.8 t	-0.1	19.7 t	19.7 t	0.0
C(3)	31.3 t	31.5 t	+0.2	32.6 t[f]	32.9 t[f]	+0.3	24.7 t	24.3 t	-0.4
C(4)	66.5 s	66.6 s	+0.1	64.6 s	64.8 s	+0.2	126.1 s	126.6 s	+0.5
C(5)	45.3 s	45.3 s	0.0	45.4 s	45.5 s	+0.1	162.1 s	162.0 s	-0.1
C(6)	73.4 d	73.6 d	+0.2	71.8 d	71.9 d	+0.1	78.3 d	78.3 d	0.0
C(7)	33.8 t	34.2 t	+0.4	32.1 t[f]	32.2 t[f]	+0.1	35.3 t	35.6 t	+0.3
C(8)	38.3 d	41.0 d	+2.7	38.1 d	40.6 d	+2.5	35.7 d	39.0 d	+3.3
C(9)	51.1 s	51.5 s	+0.4	50.8 s	51.3 s	+0.5	53.5 s	53.9 s	+0.4
C(10)	52.5 d	50.3 d	-2.2	52.9 d	50.6 d	-2.3	41.9 d	40.0 d	-1.9
C(11)	43.6 t	43.9 t	+0.3	43.1 t	43.3 t	+0.2	40.6 t	40.5 t	-0.1
C(12)	71.3 d	71.4 d	+0.1	71.5 d	71.5 d	0.0	71.9 d	72.0 d	+0.1
C(13)	125.0 s	125.6 s	+0.6	125.0 s	125.5 s	+0.5	124.9 s	125.1 s	+0.2
C(14)	107.8 d	108.0 d	+0.2	107.9 d	108.1 d	+0.2	108.0 d	108.1 d	+0.1
C(15)	144.0 d	144.2 d	+0.2	144.0 d	144.2 d	+0.2	144.2 d	144.3 d	+0.1
C(16)	139.3 d	139.1 d	-0.2	139.4 d	139.3 d	-0.1	139.6 d	139.8 d	+0.2
C(17)	16.5 q	17.0 q	+0.5	16.4 q	16.8 q	+0.4	17.0 q	16.8 q	-0.2
C(18)	48.4 t	48.2 t	-0.2	48.2 t	47.7 t	-0.5	173.0 s	173.0 s	0.0
C(19)	61.6 t	62.3 t	+0.7	61.5 t	61.7 t	+0.2			
C(20)	175.6 s	175.9 s	+0.3	175.7 s	176.0 s	+0.3	175.9 s	175.7 s	-0.2
OAc	170.3 s	170.7 s	+0.4	170.1 s	170.4 s	+0.3			
	21.2 q	21.2 q	0.0	169.8 s	169.9 s	+0.1			
				21.1 q	21.1 q	0.0			
				21.1 q	21.2 q	+0.1			

[a] In parts per million downfield from Me_4Si. Chemical shifts are accurate to ±0.05 ppm. All in $CDCl_3$ solution. All these data, except those for compound **6**, have been specially obtained by us for this work and are in complete agreement with the previously reported values.[5,8,15] [b] See note.[18] [c] $\delta_{12(R)} - \delta_{12(S)}$. [d] Taken from ref 15c,d. [e] SFORD multiplicity. [f] These assignments may be interchanged.

Table III. ^1H NMR Data of Compounds 2-7[a,b]

	2	3	4	5	6	7
H-6β	3.66 ddd (11, 4.5, 1.2)	4.76 ddd (11, 4.5, 1.1)	3.65 ddd (10.4, 3.6, 1.2)	4.79 ddd (11, 4.5, 1.2)	4.74 ddt (9, 8, 2.5)	4.75 m (18)
H-11A	2.35 d (8.5)	2.39 dd (14.0, 8.1)	2.45 dd (13.9, 8.8)	2.48 dd (13.6, 9.1)	2.56 d (8.5)	2.64 dd (14.0, 8.1)
H-11B	2.35 d (8.5)	2.36 dd (14.0, 9.0)	2.30 dd (13.9, 8.2)	2.34 dd (13.6, 7.5)	2.56 d (8.5)	2.44 dd (14.0, 9.1)
H-12	5.33 t (8.5)	5.37 t (8.5)	5.36 t (8.4)	5.38 t (8.4)	5.46 t (8.5)	5.40 t (8.5)
H-14	6.38 m (4)	6.35 m (4)	6.38 m (4)	6.35 m (4)	6.38 m (4)	6.40 m (4)
H-15	7.45 m (4)	7.43 m (4)	7.43 m (4)	7.42 m (4)	7.45 m (4)	7.43 m (4)
H-16	7.45 m (4)	7.43 m (4)	7.43 m (4)	7.42 m (4)	7.45 m (4)	7.43 m (4)
Me-17	1.03 d (7)	1.01 d (7)	1.13 d (7)	1.11 d (7)	1.08 d (6.6)	1.22 d (6.0)
H-18A[c]	2.45 d (4)	2.20 d (4.2)	2.43 d (3.6)	2.18 d (4.2)		
H-18B[d]	3.25 dd (4, 2)	2.96 dd (4.2, 2)	3.17 dd (3.6, 2.4)	2.92 dd (4.2, 2.4)		
H-19A	4.70 dd (13, 1.2)	4.46 dd (13, 1.2)	4.78 dd (13.2, 1.2)	4.50 dd (13.3, 1.2)		
H-19B	5.07 d (13)	5.21 d (13)	5.05 d (13.2)	5.30 d (13.3)		
OAc	2.02 s	2.06 s	2.07 s	2.06 s		
		1.95 s		1.95 s		

[a] Run in $CDCl_3$ solution with Me_4Si as internal standard. Chemical shifts are in ppm; figures in parentheses are coupling constants or, for nonresolved signals (m), width at half height, in both cases in Hz. [b] The spectra of all these compounds, except **7**, have been previously reported,[5-8,15] but the values given here have been newly obtained for this work. [c] Exo hydrogen with respect to ring B. [d] Endo hydrogen with respect to ring B.

Furthermore, a single-crystal X-ray determination of montanin C (**5**) was undertaken in order to elucidate its structure conclusively and to establish the difference between it and compound **3**.[5] Crystals of montanin C (**5**) have two crystallographically independent molecules, **5a** and **5b**. Both molecules are chemically identical, with the same C-12(*R*) configuration, a very similar conformation for the main skeleton of rings A, B, and C, and the same absolute stereochemistry, although the latter could not be determined by comparing only the more relevant Bijvoet pairs. The X-ray model of only one of the molecules (**5b**) is represented in Figure 1. The C-12(*R*) configuration of montanin C (**5**) was indicated by the torsion angle C(9)–C(11)–C(12)–C(13), which is of 141° and 142° for the molecules **5a** and **5b**, respectively, whereas in other neoclerodan-20,12-olide derivatives isolated from *Teucrium* species, such as capitatin, teuspinin, lolin, and chamaedroxide, it is of -103°, -140°, -125°, and -99°, respectively.[4e]

We definitely conclude, therefore, that teupolin I (**4**)[6,8] is the C-12(*R*) epimer of teucjaponin B (**2**),[5,9] and that montanin C (**5**)[7,8] is the C-12(*R*) epimer of compound **3**, previously obtained by us[5] from 19-acetylgnaphalin (**1**).

Furthermore, the rotation of the furan ring (ring D) around the C(12)–C(13) bond is different for the two molecules **5a** and **5b** of montanin C, the torsion angle O(4)–C(12)–C(13)–C(16) being of 63° for **5a** and -6° for **5b**. The conformation of the rings A, B, and C have been calculated by Cremer's method.[13] Ring C in the molecules

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Table IV. Cremer's Parameters and Torsional Angles in the Junction A/B for Molecules 1, 5a, and 5b[a]

molecule	C-12 configuration	Θ_A	ϕ_A	Q_A	τ_A	$\lvert\tau_A\rvert + \lvert\tau_B\rvert$	τ_B	Q_B	ϕ_B	Θ_B
1[4e,5]	S	6	222	0.60	-58	103	45	0.50	223	6
5a	R	9	239	0.61	-60	105	45	0.54	227	12
5b	R	9	244	0.62	-63	108	45	0.54	225	11

[a] Θ, ϕ, and τ in degrees, Q in Å.

5a and **5b** are almost E_{11} envelopes with total amplitudes of 0.20 and 0.21 Å, respectively. The Cremer's parameters, Θ, ϕ, and Q, for the six-membered rings A and B and the conformation at the junction A/B, are shown in Table IV together with the very close values of 19-acetylgnaphalin (**1**).[4e,5] In molecules 1, **5a**, and **5b** rings A and B are of the $^4C_1$ and $^6C_9$ type, respectively.

While the preceding work was being undertaken, we isolated from *Teucrium flavum* L. ssp. *glaucum* (Jordan and Fourr) Ronniger, together with other compounds,[14] a new minor diterpenic constituent, the physical and spectroscopic data of which were very similar (Table I–III) to those previously reported[15] for teucvin (**6**), another *Teucrium* diterpenoid whose structure, including its X-ray analyses,[15a,c] is well-known. Since the ^1H and ^{13}C NMR spectroscopic differences between teucvin (**6**) and the new diterpenoid (**7**) were identical with those found between teucjaponin B (**2**) and teupolin I (**4**), and also between compound **3** and montanin C (**5**) (Tables II and III), it was clear that compound **7** was the C-12(*R*) epimer of teucvin (**6**) and so, it was named 12-*epi*-teucvin.[16] Moreover, compound **7** showed an identical CD curve to that of teucvin,[15e] thus establishing the same absolute configuration for both compounds (see also the Experimental Section).

Since the pairs of isomeric neoclerodan-20,12-olide derivatives, which differ only in their configuration at C-12, seem to have very similar spectroscopic data, we were interested in finding a simple method which would allow an unambiguous determination of the configuation at C-12, even when only one of the epimers was available.

The data collected in Tables II and III provide some criteria for distinguishing the C-12 configuration of neoclerodan-20,12-olide derivatives. In fact, the compounds with a C-12(*R*) stereochemistry (**4**, **5**, and **7**) all showed the C-17 methyl protons resonance at slightly lower field than the compounds belonging to the C-12(*S*) epimeric series (**2**, **3**, and **6**), as has been pointed out previously[17] for the neoclerodan-20,12-olides 8,17-dihydroplaunolide [with a C-12(*S*) configuration] and bacchotricuneatin B [the C-12(*R*) epimer]. The ^1H NMR behavior of the C-11 methylene protons [identical, or almost identical, chemical shifts for H-11A and H-11B in the 12(*S*) compounds (**2**, **3**, and **6**) and a clear AB part of an ABX system in the 12(*R*) derivatives (**4**, **5**, and **7**), see Table III] does not provide an adequate criterion for establishing the C-12 configuration, because it can occasionally be due to the substitution pattern in the rest of the diterpenic skeleton.[4b-f,9-12,14]

Furthermore, the ^{13}C NMR spectra of these diterpenoids (**2**–**7**) showed that in compounds of the C-12(*R*) series (**4**, **5**, and **7**) the C-8 and C-9 carbon atom resonances were downfield shifted ($\Delta\delta$ +2.5 to +3.3 and +0.4 to +0.5, respectively, see Table II) and that the C-10 carbon atom resonance was upfield shifted ($\Delta\delta$ −1.9 to −2.3) with respect to those of the corresponding C-12(*S*) epimers (**2**, **3**, and **6**).[18] The small downfield shifts for the resonance of the C-13 carbon atom in the C-12(*R*) compounds ($\Delta\delta$ +0.2 to +0.6, Table II) were also of significance.

Apart from the above criteria, there is an easy and more conclusive method for establishing the C-12 configuration of neoclerodan-20,12-olide derivatives, even when only one epimer is available, namely, a NOE experiment. In compounds in which the C-12 methyne proton and the C-17 methyl protons are on the same side of the plane defined by the C(20)–C(12) lactone ring [**4**, **5**, and **7**, configuration 12(*R*)], irradiation of the C-17 methyl protons produced an 8–12% NOE enhancement of the H-12 signal, whereas this was not observed in compounds with a C-12(*S*) center (**2**, **3**, and **6**), in which H-12 and 3H-17 are on opposite sides of the plane defined by the lactone ring and, consequently, widely separated. In fact, the crystalline molecules of montanin C (**5**) showed distances between H-12 and the three H-17 atoms of 2.16, 2.20, and 2.41 Å for **5a**, and of 2.07, 2.17, and 2.21 Å for **5b**, thus explaining the observed NOE. Recently,[19c] we used this method for establishing the configuration at C-12 in some neoclerodane diterpenoids isolated from *Salvia* species.[19]

With the availability of modern analytical methods an error in the determination of structures of organic compounds is very unlikely, but there are several cases in earlier studies of *Teucrium* diterpenoids where mistakes in the assignment of the C-12 stereochemistry of these compounds may conceivably have occurred. It would seem advisable, therefore, for authors in this area to reconsider their previous assignments.[20]

Experimental Section

Melting points were determined in a Kofler apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter with a 1-dm cell. Elemental analyses were carried out in Madrid[1b] with the help of a Perkin-Elmer 240 analyzer. IR spectra were determined on a Perkin-Elmer 257 spectrometer. ^1H and ^{13}C NMR spectra were measured at 90 and 20.15 MHz, respectively, in $CDCl_3$ solution with Me_4Si as an internal standard. The proton NOE measurements were made at 80 MHz by the FT difference method with the decoupler operating in the gated

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(16) The possibility that compound **7** could be a C-6 and/or a C-10 epimer of **6** was also considered but was discarded because two of these epimers, teuflin[4a] (H-6α teucvin) and teucvidin[15e] (H-6α,H-10α teucvin), are known and they show big ^1H and ^{13}C NMR spectroscopic differences from teucvin (**6**) and 12-*epi*-teucvin (**7**), respectively.

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(18) It is noteworthy that the ^{13}C NMR data of teupolin I given in ref 8 are identical with our data[5] for teucjaponin B[9] (**2**) and that the ^1H NMR data of teupolin I given in ref 6 do not agree with those given in ref 8. It is to be assumed that the sample named teupolin I was not the same compound in the two articles. In view of the present evidence, the sample was probably teupolin I (**4**) in ref 6 and teucjaponin B[5,9] (**2**) in ref 8.

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(20) A careful review of the C-12 stereochemistry of some of the neoclerodane diterpenoids earlier isolated by us[1b,c] from *Teucria* will be published elsewhere.

mode. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6MG instrument.

For more spectroscopic data (IR, UV, and mass spectra) of the previously described compounds (**2–6**) see references[5-12,15] and notes.[18]

X-ray Structure Determination of Montanin C (5). $C_{24}H_{30}O_8$ crystallized in the space group $P2_1$ with $Z = 4$ and $a = 16.748$ (2) Å, $b = 11.777$ (1) Å, and $c = 12.634$ (1) Å and $\beta = 111.78$ (1)°. The molecular weight is 446.48, and the calculated density is 1.275 g cm^{-3}. The intensities of the 2929 independent Friedel pairs to $\Theta = 60°$ were alternately collected on an automated four-circle diffractometer. The single crystal used, of section ~0.2 mm, decomposed during the experiment, showing an intensity decay of 23% for graphite-monochromated Cu Kα radiation (1.5418 Å). Some experimental details are as follows: $\omega/2\Theta$ scan mode; 1.20° scan width; 0.040 s g^{-1} scan speed with the same measurement time for both backgrounds as for the peak. After the usual correction for Lorentz and polarization effects, 2368 Friedel pairs were considered as observed, when $I > 2\sigma(I)$, and were used for the structure determination and refinement. No absorption correction was applied ($\mu = 7.58$ cm^{-1}). The atomic scattering factors and the anomalous dispersion corrections were taken from the literature.[21] The structure was solved by MULTAN[22] and refined by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms, except those of the three methyl groups, found in a Fourier difference map were included as fixed isotropic contributors in the refinement.

A weighting scheme was selected to prevent bias in $\langle\omega\Delta^2F\rangle$ vs. $\langle|F_o|\rangle$ and $\langle\sin\Theta/\lambda\rangle$. Several cycles of weighted anisotropic refinement, including both hkl and $\bar{h}\bar{k}\bar{l}$ reflections, gave the following unweighted and weighted discrepancy indices: $R = 0.066$ and $R_w = 0.069$.[23]

The absolute configuration of montanin C could not be determined, either, by comparing only the more relevant Bijvoet pairs. Figure 1 shows the X-ray molecular model of one (**5b**) of the two crystallographically independent molecules, assuming a neoclerodane[3a] absolute configuration, which, furthermore, is the one predicted when comparing the [α] values of compound **3** ([α]$_D$ +33.5, [α]$_{578}$ +35.3, [α]$_{546}$ +39.9, [α]$_{436}$ +66.2, [α]$_{365}$ +100.3 (*c* 0.97, $CHCl_3$)) with those of montanin C (**5**, [α]$_D$ +7.4, [α]$_{578}$ +8.1, [α]$_{546}$ +9.2, [α]$_{436}$ +13.1, [α]$_{365}$ +23.1 (*c* 0.89, $CHCl_3$)).

Isolation of 12-*epi*-Teucvin (7). Dried and finely powdered *Teucrium flavum* L. ssp. *glaucum* (Jordan and Fourr) Ronniger (aerial parts, 900 g), collected on the Gennargentu mountains, Sardinia (Italy), were extracted with acetone, as previously described.[14] The chromatographic fraction (450 mg) obtained before elution of teuflavin[14] was repeatedly chromatographed over silica gel columns eluted with petroleum ether–EtOAc (1:1), yielding pure 12-*epi*-teucvin (**7**): 290 mg; mp and [α]$^{17}_D$ see Table I; IR (KBr) 3160, 3140, 3120, 2980, 2940, 2920, 2880, 2870, 2860, 1760, 1740, 1690, 1610, 1508, 1470, 1440, 1385, 1360, 1350, 1330, 1315, 1280, 1220, 1200, 1175, 1155, 1050, 1030, 1025, 975, 945, 880, 805, 745 cm^{-1}; UV (EtOH) λ_{max} 224 nm (log ϵ 4.00); ^{1}H NMR see Table III; ^{13}C NMR see Table II; mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 328 (M^+, 20), 310 (45), 299 (25), 238 (15), 265 (5), 234 (15), 229 (20), 201 (10), 179 (25), 178 (22), 161 (17), 150 (32), 136 (30), 117 (15), 115 (15), 108 (16), 107 (20), 105 (35), 96 (48), 95 (100, base peak), 94 (50), 91 (47), 81 (50), 79 (58), 77 (55), 69 (25), 65 (27), 53 (30); CD nm ([Θ]) 281 (0), 231 (+65 000), 220 (0), 212 (−24 000), 210 (−20 000) (*c* 0.218, dioxane). [For the CD data of teucvin (**6**) see ref 15e.] Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.77; H, 6.25.

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Supplementary Material Available: A list of atomic parameters, bond distances, bond angles, torsion angles, and conformational analysis for the rings (17 pages). Ordering information is given on any current masthead page.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Cannabichromene, Cannabicitran, and Cannabicyclol and Their Analogues

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Carbon-13 nuclear magnetic resonance spectra have been recorded for cannabichrome, cannabicitran, and cannabicyclol and their analogues. The absorptions have been assigned to specific carbons with the aid of off-resonance, selective proton decoupling, ^{13}C J_R vs. ^{1}H δ's, and chemical shift comparison with model compounds.

Despite the wide variety of ring systems isolated[1] from the plant *Canabis sativa* L, only three reports concerning ^{13}C NMR spectra of cannabinoids have been published.[2-4] These studies were largely limited to Δ^8-, Δ^9-tetrahydrocannabinols and related model compounds[2,3] and cannabidiol.[4] Apparently, ^{13}C NMR spectra of cannabichromene (**1**, R = H; $R_1 = C_5H_{11}$)[5-7] and other conforma-

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