The planar residues of the α and ω chains form dihedral angles of 52·3 (6) and 44·0 (8)°, respectively, with the basal plane of the five-membered ring [defined by the non-H atoms C(8) through C(11)].

The bond lengths, bond angles and · thermal parameters for the atoms of the α chain, the five-atom ring and the unsaturated portion of the ω chain show no unusual features. However, the thermal parameters and the bond lengths for the terminal n-pentyl segment of the ω chain display significant effects of high thermal motion (even at 173 K). The magnitude and direction of the thermal ellipsoids of atoms C(16) through C(20) are consistent with either static or dynamic torsional disorder about the C(14)—C(15) bond. Owing to this high thermal motion, the H atoms of the terminal C atom, C(20), of the ω chain were not located and the C(19)—C(20) bond length is foreshortened to 1·208 (13) Å.

The stereoscopic view shown in Fig. 2 reveals that the molecular packing is dominated by strong H bonds between the carboxyl groups of adjacent molecules. The pertinent contact distances are H(2)···O'(1) = 1·93 (5) and O(1)···O'(2) = 2·652 (4) Å. The oxygen atoms of the two ketone residues are not involved in H bonds. This H-bonding pattern is consistent with the fact that the 7ME1 molecule has a deficiency of H-bond donors (the carboxylic OH group) relative to H-bond acceptors (the three carbonyl O atoms). The natural prostaglandin molecules have a better balance of H-bond donor and acceptor groups by having two or three alcoholic hydroxyl groups that can function simultaneously as H-bond donors and acceptors and frequently participate in bifurcated H bonds.

References

DeTitta, G. T., Langs, D. A. & Edmonds, J. W. (1979). Biochemistry, 18, 3387–3391.
DeTitta, G. T., Langs, D. A., Edmonds, J. W. & Duax, W. L. (1980). Acta Cryst. B36, 638–645.
Edmonds, J. W. & Duax, W. L. (1975). J. Am. Chem. Soc. 97, 413–417.
Ibers, J. A. & Hamilton, W. C. (1974). International Tables for X-ray Crystallography, Vol. IV, pp. 72–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Matthews, R. S. (1985). In preparation.
Oliver, J. D. & Strickland, L. C. (1983). Acta Cryst. C39, 380–383.
Sheldrick, G. M. (1984). SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Nicolet XRD Division, Madison, WI.
Spek, A. L. (1977). Acta Cryst. B33, 816–824.

Structure of 2-Methyl-6-(4-methyl-2-oxo-3-cyclohexen-1-yl)hept-2-enoic Acid, a Natural 1-Bisabolone

By Hans Preut,* Wolfgang Kreiser and Thomas Müller

Fachbereich Chemie der Universität Dortmund, Postfach 500500, D-4600 Dortmund 50, Federal Republic of Germany

and Peter G. Jones

Anorganisch Chemisches Institut der Universität Göttingen,. Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

Abstract. $C_{15}H_{22}O_3$, $M_r = 250·34$, orthorhombic, $P2_12_12_1$, $a = 8·109$ (3), $b = 11·806$ (4), $c = 15·132$ (4) Å, $U = 1448·7$ (8) Å³, $Z = 4$, $D_x = 1·148$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·08$ mm⁻¹, $F(000) = 544$, $T = 294$ (1) K, final $R = 0·055$ for 899 unique diffractometer data and 164 refined parameters. The relative configuration of a natural 1-bisabolone is shown to be $6R,7S$. In the crystal the molecules are linked by H bonds to form chains parallel to **b** [O···O 2·709 (4), H···O 1·760 (3) Å, ∠C—O—H 115·1 (4)°].

Introduction. During the last decade an increasing number of sesquiterpenoids, representing the skeleton of 1-bisabolone (1), have been isolated from various plant sources, mainly by F. Bohlmann. Among these are (1), itself, from Stevia purpurea Pers. (Bohlmann, Zdero & Schöneweiss, 1976), (2) from Ptilostemon chamaepeuce Less. (Bohlmann, Rao & Schwarz, 1974), (3) from Stevia ovata Willd. (Bohlmann, Suwita, Natu, Czerson

* To whom correspondence should be addressed.

& Suwita, 1977) and (4) from *Baeria chrysostoma* (Bohlmann & Zdero, 1978). Moreover, these are sometimes accompanied by aromatic compounds with the same framework, like α-curcurmene, nuciferol, curcuphenol and curcuquinone. The latter do not cause any serious problems, neither in synthesis, nor from the viewpoint of stereochemistry, since only one chiral center is involved. On the other hand, formulas (1)–(4) display two chiral atoms, at least. But apparently all the above natural sources produce only one single, optically active diastereomer. Indeed determination of the relative configuration at the adjacent chiral C atoms [C(6) and C(7)] in this series proves to be a challenging task, and was tentatively undertaken by Bohlmann *et al.* (1976), referring to the corresponding ^{1}H NMR spectra. Starting with optically active citronellol in our group we succeeded in synthesizing the natural products mentioned and their appropriate diastereomers. In all cases both the configurational isomers had significantly different chemical shifts for the methyl doublet at C(7). Although this proved quite helpful during their separation and for the assignment to the stereochemical series in common, we were not able to provide a reliable configuration. All substances from nature have been isolated in an oily state; and it was several years before we succeeded in preparing a solid derivative, due to the extreme inertness of the carbonyl function within the six-membered ring. At last (4a) was successfully fractionated into an oily and a crystalline part melting at 395–397 K.

(1)

(2)

(3)

(4) *R* – CH₃
(4a) *R* - H
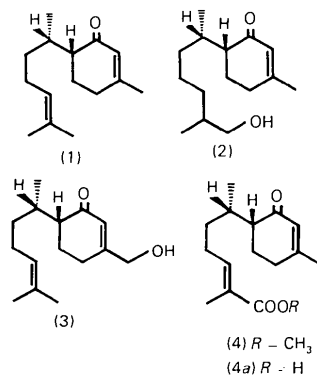
Experimental. Crystals of (4a) were grown very slowly from an ethyl acetate solution at ambient temperature, while the solvent simultaneously evaporated. Thus the crystalline optically active acid (4a) and its racemate were generated. In either case the same diastereomer was isolated, whereas the second isomer remained an oil. $\omega/2\theta$ scan, scan speed 0·8–2·5° min^{-1} in θ; Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; crystal 0·4 × 0·2 × 0·4 mm; lattice parameters from least-squares fit with 25 reflexions up to 2θ = 24·6°; six standard reflexions recorded every 2 h: only random deviations; 2842 reflections measured;

$2° \le \theta \le 24°$, $0 \le h \le 9$, $0 \le k \le 14$, $-18 \le l \le 18$; after averaging $(R_{int} = 0·02)$: 899 unique observed reflections with $I > 2\sigma(I)$, 431 unobserved; Lorentz–polarization but no absorption correction; systematic absences $h00$: $h = 2n + 1$, $0k0$: $k = 2n + 1$, $00l$: $l = 2n + 1$, space group $P2_12_12_1$; structure solved by multisolution tangent refinement with *SHELXTL* (Sheldrick, 1981), ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C–H 0·95 Å, H–C–H 109·5° in CH₂ and CH₃ groups, C–C–H equal) with the *Enraf-Nonius Structure Determination Package* (Frenz, 1981); complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); least-squares refinement based on F and 164 refined parameters; $w^{-1} = [\sigma^2(I) + (0·06F_o^2)^2]^{1/2}$; $S = 1·42$, $R = 0·055$, $wR = 0·083$, $(\Delta/\sigma)_{max} = 0·11$; no significant features in a final ΔF synthesis: maximum peak 0·21 (7) e Å^{-3}; drawings with *ORTEP*II (Johnson, 1976) and *POP*1 (van de Waal, 1976).

Discussion. The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the packing is in Fig. 2. Positional parameters and the equivalent isotropic values of the anisotropic temperature factors β_{ik} for the non-hydrogen atoms are given in Table 1.* Bond lengths and angles are given in Table 2. The asymmetric unit contains one molecule. The X-ray investigation of (4a) (m.p. 395–397 K) clearly demonstrates the 6*R*,7*S* configuration, now related with the high-field NMR signal at $\delta = 0·82$; whereas the oily diastereomer resonates at $\delta = 0·96$.

A short intermolecular O···O distance [O(1)-$(x,y-1,z)$···O(2)(x,y,z) 2·709 (4) Å] indicates an H bond. If one places the H atom bound to O(2) on the line connecting O(1)$(x,y-1,z)$ and O(2)(x,y,z) at a distance of 0·95 Å from atom O(2) the following distance and angle result: H[O(2)]···O(1)$(x,y-1,z)$ 1·760 (3) Å and C(12)–O(2)–H[O(2)] 115·1 (4)°. These values agree with those in 3,3'-thiodipropionic acid (Prout & Hernandez-Cassou, 1982): O···H 1·74 (3) Å, C–O–H 113 (2)°. The bond distances C(2)–C(3) and C(10)–C(11) show double-bond character and the neighboring bonds C(1)–C(2), C(3)–C(4), C(9)–C(10) and C(11)–C(13) are shorter than single bonds. Least-squares planes through the atoms C(9), C(10), C(11), C(12), C(13), O(2), O(3) [(A) 0·986x +0·168y −0·004z = −3·400 Å] (x,y,z are orthogonalized coordinates with x along **a**, y in the

plane *ab* and *z* along c^*); maximum deviation of an atom from the plane 0·067 (5) Å], through C(6), C(7), C(8), C(9), C(10) [(*B*) 0·044*x* −0·163*y* −0·986*z* = 6·746 Å; 0·113 (5) Å] and through C(1), C(2), C(3), C(4), C(6), C(15), O(1) [(*C*) −0·305*x* +0·047*y* −0·951*z* = 6·693 Å; 0·048 (4) Å] show that these groups are nearly planar. The dihedral angles between these planes are: (*A*)/(*B*) 88·9 (5), (*A*)/(*C*) 106·8 (5), (*B*)/(*C*) 23·6 (5)°. In the six-membered ring the dihedral angle between the nearly planar part through the atoms C(1), C(2), C(3), C(4), C(6) [see plane (*C*)] and the plane through the atoms C(1), C(5), C(6) is 46·6 (5)°. The ring has a local pseudo mirror along C(5)⋯C(2). There are no interactions between the chains exceeding van der Waals forces.
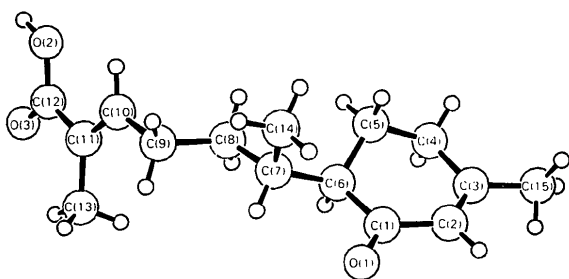
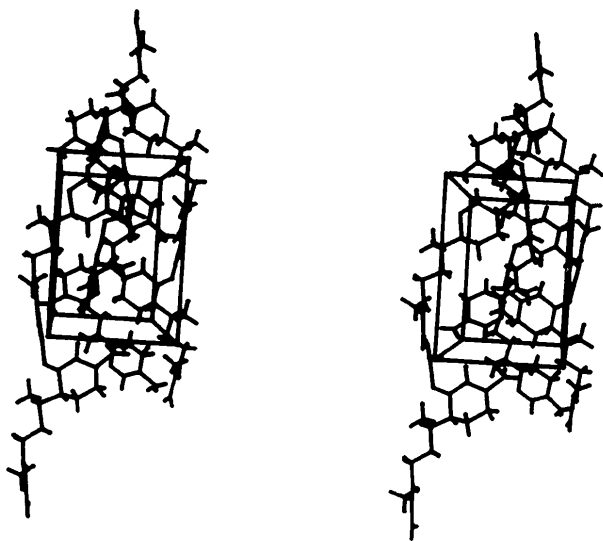Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
O(1)	0·4658 (5)	0·8367 (3)	0·4174 (3)	7·33 (9)
O(2)	0·4054 (6)	0·0624 (2)	0·4187 (3)	7·3 (1)
O(3)	0·4241 (6)	0·0543 (3)	0·5620 (3)	8·0 (1)
C(1)	0·5970 (7)	0·7965 (3)	0·3922 (3)	5·0 (1)
C(2)	0·7368 (7)	0·8674 (3)	0·3705 (3)	5·4 (1)
C(3)	0·8837 (7)	0·8258 (4)	0·3451 (3)	5·7 (1)
C(4)	0·9094 (8)	0·7026 (4)	0·3332 (3)	6·0 (1)
C(5)	0·7483 (7)	0·6393 (3)	0·3191 (3)	5·0 (1)
C(6)	0·6211 (6)	0·6687 (3)	0·3876 (3)	4·41 (9)
C(7)	0·4583 (6)	0·6052 (3)	0·3795 (3)	4·9 (1)
C(8)	0·4860 (7)	0·4784 (3)	0·3948 (3)	5·4 (1)
C(9)	0·3287 (8)	0·4133 (4)	0·4135 (4)	6·8 (1)
C(10)	0·3595 (7)	0·2914 (3)	0·4237 (3)	5·7 (1)
C(11)	0·3700 (7)	0·2313 (4)	0·4985 (4)	5·0 (1)
C(12)	0·4025 (6)	0·1090 (3)	0·4968 (3)	4·9 (1)
C(13)	0·353 (1)	0·2813 (4)	0·5894 (4)	9·0 (2)
C(14)	0·3722 (7)	0·6287 (4)	0·2921 (4)	6·7 (1)
C(15)	1·0279 (8)	0·8993 (5)	0·3261 (5)	8·8 (2)

Fig. 1. General view of the molecule.

Fig. 2. Stereoscopic view of the packing (molecules are linked *via* an H bridge).

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)–C(2)	1·447 (7)	C(7)–C(8)	1·531 (5)
C(1)–O(1)	1·226 (7)	C(7)–C(14)	1·520 (8)
C(1)–C(6)	1·522 (5)	C(8)–C(9)	1·516 (8)
C(2)–C(3)	1·344 (8)	C(9)–C(10)	1·469 (6)
C(3)–C(4)	1·481 (6)	C(10)–C(11)	1·338 (7)
C(3)–C(15)	1·484 (8)	C(11)–C(12)	1·468 (6)
C(4)–C(5)	1·520 (7)	C(11)–C(13)	1·503 (8)
C(5)–C(6)	1·504 (7)	C(12)–O(2)	1·304 (6)
C(6)–C(7)	1·523 (7)	C(12)–O(3)	1·192 (6)
O(1)–C(1)–C(2)	121·8 (4)	C(6)–C(7)–C(14)	112·2 (4)
O(1)–C(1)–C(6)	120·6 (4)	C(6)–C(7)–C(8)	110·0 (4)
C(2)–C(1)–C(6)	117·6 (4)	C(14)–C(7)–C(8)	112·2 (4)
C(1)–C(2)–C(3)	123·2 (4)	C(7)–C(8)–C(9)	113·6 (4)
C(2)–C(3)–C(4)	121·2 (5)	C(8)–C(9)–C(10)	111·9 (5)
C(2)–C(3)–C(15)	122·7 (4)	C(9)–C(10)–C(11)	128·2 (5)
C(4)–C(3)–C(15)	116·1 (5)	C(10)–C(11)–C(12)	121·2 (4)
C(3)–C(4)–C(5)	112·3 (5)	C(10)–C(11)–C(13)	124·1 (4)
C(4)–C(5)–C(6)	112·3 (4)	C(12)–C(11)–C(13)	114·7 (4)
C(5)–C(6)–C(1)	110·4 (3)	C(11)–C(12)–O(2)	115·7 (4)
C(5)–C(6)–C(7)	115·1 (3)	C(11)–C(12)–O(3)	123·1 (4)
C(1)–C(6)–C(7)	112·4 (4)	O(2)–C(12)–O(3)	121·2 (4)

References

BOHLMANN, F., RAO, N. & SCHWARZ, H. (1974). *Chem. Ber.* **107**, 650–653.

BOHLMANN, F., SUWITA, A., NATU, A. A., CZERSON, H. & SUWITA, A. (1977). *Chem. Ber.* **110**, 3572–3581.

BOHLMANN, F. & ZDERO, CH. (1978). *Phytochemistry*, **17**, 2032–2033.

BOHLMANN, F., ZDERO, CH. & SCHÖNEWEISS, S. (1976). *Chem. Ber.* **109**, 3366–3370.

FRENZ, B. A. (1981). *Enraf–Nonius Structure Determination Package*, 4th ed., version 18.

International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

PROUT, K. & HERNANDEZ-CASSOU, S. (1982). *Acta Cryst.* B**38**, 338–340.

SHELDRICK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen.

WAAL, B. W. VAN DE (1976). *POPI*. Twente Univ. of Technology, The Netherlands.