The Crystal Structure of Levopimaric Acid, $C_{20}H_{30}O_2$
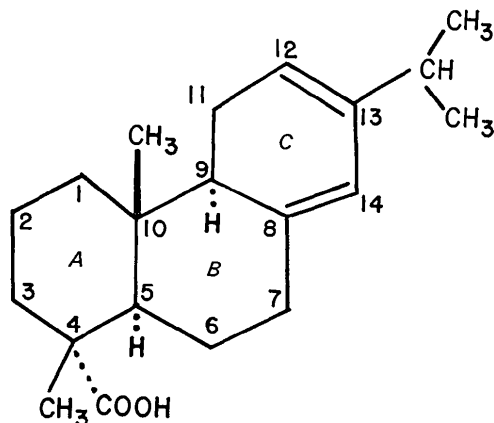
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Levopimaric acid, one of the components of rosin, is an optically active carboxylic acid which forms a dimer by hydrogen bonding between the carboxyl groups of two independent molecules in the asymmetric unit. The $-C\langle\begin{smallmatrix}O\cdots HO\\OH\cdots O\end{smallmatrix}\rangle C-$ group is nearly planar and the $OH\cdots O$ bond lengths are 2·644 and 2·628 Å (e.s.d. 0·006 Å). The crystal-structure analysis confirms that the molecule has a folded conformation between rings *B* and *C* and that the diene system is twisted as postulated from the large negative Cotton effect. The torsional angle between the two double bonds in the *C* ring is $-9\cdot1°$ and $-11\cdot8°$ for the two independent molecules. The material crystallizes in space group $P2_12_12_1$ with $a = 15\cdot664 \pm 0\cdot003$, $b = 19\cdot387 \pm 0\cdot005$, $c = 11\cdot851 \pm 0\cdot002$ Å, and $Z = 8$. The R value for 3317 reflections is 6·0 %. Phases were determined directly from the structure-factor magnitudes by the symbolic addition procedure.

Introduction

Rosin, the nonvolatile residue obtained from the clear oleoresin which exudes from incisions cut into the bark of living pine trees, is a mixture of several isomeric diterpenoid acids. Levopimaric acid,

one of the components of rosin, differs from neoabietic acid, abietic acid, and palustric acid only in the locations of the two double bonds. Pimaric acid and isopimaric acid both have a $-CH_3$ and a $-CH = CH_3$ group on C(13) rather than an isopropyl group.

The stereochemistry and absolute configuration of levopimaric acid have been determined by chemical and spectroscopic means (Schuller & Lawrence, 1961; Burgstahler, Ziffer & Weiss, 1961; Weiss, Ziffer & Charney, 1962; Dauben & Coates, 1963). Repulsive forces between the two axial CH_3 groups on C(4) and C(10), as well as between the CH_3 group on C(10) and H(11β), could be expected to distort the six-membered rings. A nonplanar diene system and a fold between the B/C rings have been proposed in order to correlate these structural features with the relatively large neg-

ative Cotton effect ($\Delta\varepsilon = -12\cdot2$ from circular dichroism measurements) exhibited by levopimaric acid (Burgstahler *et. al.,* 1961; Weiss *et. al.,* 1962; Burgstahler, Gawronski, Niemann & Feinberg, 1971). The purpose of the present investigation was to confirm the proposed conformation of this molecule (Weiss, Karle & Whalley, 1971).

The crystal-structure determination brought to light another interesting feature: there are two independent molecules of levopimaric acid in the asymmetric unit. These optically active molecules form a dimeric unit through two $OH\cdots O$ bonds between the carboxyl groups. Although the formation of dimers is a common occurrence for carboxylic acids when they crystallize in centrosymmetric space groups, to the author's knowlegde this is the second reported occurrence of dimer formation in a noncentrosymmetric space group, the other case being tartronic acid, $COOH.CH(OH)COOH$ (van Eijck, Kanters & Kroon, 1965), and the first case of dimer formation in an optically active acid.

Experimental

Crystals of levopimaric acid were provided by Dr Ulrich Weiss of the National Institutes of Health. Intensity data were collected on a four-circle automatic diffractometer using the $\theta-2\theta$ scan technique with a $2\cdot0°+2\theta(\alpha_2)-2\theta(\alpha_1)$ scan over 2θ. Background counts were measured for 10 sec at either end of the scan. The intensities were corrected for Lorentz and polarization factors, and normalized structure factors $|E|$ were derived. Cell parameters and other physical data are listed in Table 1.

Phases were derived directly from the normalized structure-factor magnitudes by means of the symbolic addition procedure for noncentrosymmetric crystals (Karle & Karle, 1966). The origin and enantiomorph were specified by assigning the phase $+\pi/2$ to the re-

Table 1. *Physical data*

Molecular formula	$C_{20}H_{30}O_2$
Molecular weight	302·44
Melting point	150°C
Habit	Stout prismatic
Crystal size	$1\cdot0 \times 0\cdot7 \times 0\cdot5$ mm
Space group	$P2_12_12_1$
a	$15\cdot664 \pm 0\cdot003$ Å
b	$19\cdot387 \pm 0\cdot005$
c	$11\cdot851 \pm 0\cdot002$
V	$3599\cdot1$ Å^3
Z	8 molecules per unit cell
Density (calculated)	$1\cdot116$ g.cm^{-3}
Radiation	Cu $K\alpha$ (Ni filter)
Wavelength	$1\cdot54178$ Å
Linear absorption coefficient	$5\cdot57$ cm^{-1}
Number of independent reflections	3317

flections 310, 012, 301 and 073. Three other reflections were assigned symbolic phases to implement the sum-of-angles formula. They were $1,14,3$ (m), $2,16,3$ (p) and 802 ($a=0$ or π). In the course of phase determition, it became apparent that m had a value near 0 and that p was near $\pm \pi/2$. About 50 phases obtained with the sum-of-angles formula were refined, and phases for additional reflections with $|E| > 1:1$ were obtained with the tangent formula (Karle & Hauptman, 1956). An E map computed with 908 reflections with $|E| > 1\cdot1$ for the assignment $a=\pi$, $m=0$, and $p=+\pi/2^*$ had 20 large peaks. Nine of these peaks represented adjacent atoms in one independent molecule, whereas the other 11 peaks represented atoms in three unconnected segments of the second molecule. The remaining atoms were found using one cycle of a recycling procedure based on the partial structure (Karle, 1968).

Coordinates and thermal parameters were refined by full-matrix least-squares methods, using program *ORFLS* of Busing, Levy & Martin (1962). Isotropic refinement on the 44 carbon and oxygen atoms reduced the R value to $16\cdot9\%$ for all the data. To conserve computing time for the anisotropic refinement, which involves 397 parameters, only the 2132 data with $|F_o| > 5\cdot0$ were used for all the cycles except the final one. The weighting function used was $w=20/|F_o|$ for $|F_o| > 20$ and $w=1$ otherwise. A difference map at $R = 9\cdot0$ contained 39 distinct peaks which represented hydrogen atoms. Coordinates for the remainder of the hydrogen atoms (except the two associated with the carboxyl groups) were assumed. The assumed coordinates are marked by a dagger in Table 2. Thermal parameters for the H atoms were assumed to be the same as for the C atom to which they are attached. Further anisotropic least-squares refinement with the H parameters kept constant reduced the R value for the data with

$|F_o| > 5\cdot0$ to $4\cdot7\%$. One final cycle of refinement with all 3317 data resulted in $R=6\cdot0\%$. In the last cycle of refinement, using all the data, the magnitude of the shifts was approximately the same as the errors. The errors were about $\frac{2}{3}$ the magnitude of those obtained in the refinement with the incomplete set of data.

Table 2. *Approximate coordinates for hydrogen atoms*

	x	y	z
H(1–1)	0·292	0·433	0·462
H(1–2)	0·258	0·358	0·483
H(2–1)	0·405	0·407	0·325
H(2–2)	0·428	0·370	0·433
H(3–1)	0·428	0·278	0·292
H(3–2)	0·350	0·267	0·383
H(5)	0·208	0·288	0·333
H(6–1)	0·158	0·370	0·117
H(6–2)	0·145	0·280	0·125
H(7–1)	0·008	0·333	0·158
H(7–2)	0·050	0·292	0·283
H(9)	0·138	0·360	0·445
H(11–1)†	0·182	0 448	0·540
H(11–2)†	0·181	0·480	0·493
H(12)	0·092	0·583	0·467
H(14)	−0·028	0·450	0·192
H(16–1)	0·292	0·345	0·062
H(16–2)	0·395	0·317	0·092
H(16–3)	0·350	0·390	0·133
H(17–1)	0·233	0·500	0·292
H(17–2)	0·180	0·464	0·191
H(17–3)	0·300	0·460	0·213
H(18)	−0·092	0·575	0·262
H(19–1)†	−0·065	0·687	0·303
H(19–2)†	−0·073	0·629	0·418
H(19–2)†	0·027	0·663	0·380
H(20–1)†	0·003	0·650	0·119
H(20–2)†	0 037	0·564	0·103
H(20–3)†	0·097	0·622	0·185
H(1*–1)	0·145	0·778	0·127
H(1*–2)	0·128	0·854	0·203
H(2*–1)	0·163	0·850	−0·042
H(2*–2)	0·083	0·862	0·008
H(3*–1)	0·165	0·976	−0·039
H(3*–2)	0·135	0·972	0·104
H(5*)	0·250	0·928	0 242
H(6*–1)	0·425	0·892	0·167
H(6*–2)	0·395	0·962	0·217
H(7*–1)	0·450	0·892	0·367
H(7*–2)	0·343	0·905	0·403
H(9*)	0·233	0·839	0·345
H(11*–1)†	0·194	0·728	0·389
H(11*–2)	0·178	0·725	0·225
H(12*)†	0·272	0·622	0·320
H(14*)†	0·470	0·762	0·360
H(16*–1)	0·393	0·955	−0·025
H(16*–2)	0·322	0·972	−0·075
H(16*–3)	0·325	0·895	−0·067
H(17*–1)	0·303	0·750	0·092
H(17*–2)	0·375	0·792	0·100
H(17*–3)	0·312	0·809	0·007
H(18*)†	0·498	0·649	0·421
H(20*–1)†	0·555	0·589	0·254
H(20*–2)†	0·529	0·677	0 228
H(20*–3)†	0·460	0·611	0·180

†Assumed coordinates.

Observed and calculated structure factors are listed in Table 3. Coordinates and thermal parameters for the C and O atoms are listed in Table 4.

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* The phases listed in Table 3 do not correspond to the initial phases. Once the structure was known, it was found necessary to change the hand of the molecule, and it was also desirable to change the origin for better placement of the molecules.

THE CRYSTAL STRUCTURE OF LEVOPIMARIC ACID

Table 3. Observed and calculated structure factors

The columns represent the index k, $10|F_o|$, $10|F_c|$, and the phase in cycles ($\times 100$).

Discussion

The configuration of the two independent molecules of levopimaric acid is shown in the stereodiagram in Fig. 1. The two molecules exist as a dimer by the formation of two hydrogen bonds of lengths 2·644 and 2·628 Å between their carboxyl groups. They are related very approximately by a twofold axis, which is skewed with respect to the cell edges. The formation of a dicarboxylic dimer in a noncentrosymmetric space

Table 3 (*cont.*)

6	39	37	71
9	90	91	54
10	101	100	30
11	65	50	5
12	125	130	15
13	23	23	65
14	0	14	68
15	28	29	16
6	K	10	
0	24	22	50
1	51	62	27
2	156	156	38
3	37	36	81
4	92	102	24
5	21	31	98
6	54	48	4
7	19	19	96
8	29	32	91
9	67	59	92
10	97	87	80
11	29	27	25
12	39	28	17
13	9	11	68
6	K	11	
0	127	119	75
1	43	35	30
2	58	50	3
3	41	45	59
4	60	64	89
5	25	33	61
6	47	36	43
7	59	57	19
8	50	53	6
9	22	26	7
10	58	62	86
11	33	30	61
6	K	12	
0	30	38	50
1	29	38	80
2	48	41	41
3	38	47	55
4	27	34	4
5	81	75	48
6	56	62	28
7	38	29	40
8	39	34	21
6	K	13	
0	20	3	25
7	K	0	
1	73	71	75
2	99	110	25
3	83	80	25
4	29	7	25
5	47	14	75
6	13	34	25
7	290	292	75
8	7	24	75
9	85	99	25
10	216	217	75
11	162	154	75
12	8	9	25
13	115	107	25
14	79	82	25
15	123	122	25
16	14	7	75
17	33	42	75
18	4	8	25
19	13	19	25
20	46	48	25
7	K	1	
0	244	266	25
1	506	498	89
2	251	254	8
3	136	126	28
4	174	168	20
5	145	163	43
6	97	105	74
7	123	120	28
8	223	222	91
9	148	143	29
10	130	126	95
11	130	120	27
12	19	4	98
13	19	13	97
14	30	38	58
15	119	126	68
16	57	52	58
17	31	36	61
18	18	14	74
19	36	39	18
20	20	21	97
7	K	2	
0	643	667	50
1	583	625	25
2	589	604	90
3	208	196	87
4	163	148	1
5	145	129	34
6	60	57	15
7	233	237	78
8	48	61	71
9	192	198	76
10	149	147	53
11	53	50	38
12	131	142	82
13	128	125	80
14	105	97	68
15	76	59	22
16	82	87	29
17	71	69	45
18	25	29	18
19	37	36	39
20	42	42	54
7	K	3	
0	400	394	25
1	82	67	28
2	114	107	33
3	141	158	41
4	193	179	80
5	46	46	76
6	107	122	76
7	216	211	70
8	80	77	39
9	144	140	95
10	55	33	59
11	71	62	18
12	82	85	44
13	116	118	44
14	71	86	86
15	157	154	15
16	65	66	63
17	42	37	93
18	64	62	32
19	31	31	54
20	26	31	62
7	K	4	
0	22	12	50
1	339	322	4
2	275	279	45
3	310	318	17
4	126	128	44
5	265	234	77
6	80	93	23
7	113	106	24
8	164	160	96
9	70	67	84
10	297	295	82
11	231	234	90
12	39	33	34
13	60	60	19
14	165	159	28
15	63	54	60
16	113	112	86
17	70	69	37
18	23	24	55
19	13	2	74
7	K	5	
0	45	42	25
1	116	114	47
2	50	50	31
3	275	265	81
4	16	20	7
5	99	98	67
6	263	264	94
7	172	179	11
8	167	113	91
9	127	143	27
10	76	88	23
11	116	118	54
12	186	187	80
13	97	103	2
14	211	213	46
15	101	103	79
16	82	83	19
17	29	23	77
18	44	46	65
19	53	55	51
7	K	6	
0	76	72	0
1	141	140	52
2	66	74	9
3	18	18	67
4	126	131	35
5	41	56	4
6	40	31	35
7	34	20	75
8	95	99	81
9	262	261	94
10	233	248	31
11	25	11	55
12	71	67	4
13	60	68	43
14	114	116	68
15	35	38	42
16	29	16	41
17	29	30	18
18	75	75	85
7	K	7	
0	122	123	25
1	86	88	72
2	95	97	95
3	125	121	40
4	140	143	89
5	126	132	11
6	130	133	36
7	34	28	24
8	36	49	44
9	35	38	14
10	84	87	79
11	123	125	8
12	65	59	29
13	0	16	61
14	38	39	9
15	30	30	12
16	24	28	48
17	49	45	55
7	K	8	
0	66	67	50
1	86	101	18
2	214	219	42
3	51	49	16
4	58	73	5
5	55	69	70
6	132	136	6
7	55	55	17
8	143	142	33
9	84	88	59
10	106	124	92
11	46	31	89
12	0	10	30
13	58	46	69
14	77	71	2
15	23	18	75
16	33	39	65
7	K	9	
0	57	54	75
1	57	54	23
2	52	60	11
3	64	75	91
4	125	118	47
5	83	85	63
6	29	28	80
7	68	75	13
8	47	44	14
9	27	34	50
10	29	32	61
11	61	63	29
12	46	47	43
13	11	17	15
14	26	21	16
7	K	10	
0	73	74	50
1	77	72	71
2	25	24	69
3	100	99	65
4	52	50	26
5	75	80	42
6	84	79	52
7	8	4	47
8	57	61	15
9	88	91	20
10	53	44	9
11	27	35	30
12	61	52	66
7	K	11	
0	54	49	25
1	18	5	59
2	28	18	29
3	34	46	37
4	57	69	5
5	13	18	9
6	18	20	46
7	37	36	54
8	37	38	63
9	70	64	17
10	40	33	34
7	K	12	
0	8	3	0
1	52	49	74
2	18	15	80
3	24	15	91
4	63	64	72
5	36	30	33
6	34	33	18
8	K	0	
0	290	284	0
1	205	192	0
2	90	111	0
3	205	197	0
4	118	110	50
5	77	86	50
6	178	202	0
7	41	17	0
8	50	34	50
9	29	39	0
10	36	44	50
11	23	14	50
12	89	87	50
13	122	123	0
14	201	208	50
15	104	109	50
16	86	85	0
17	76	76	50
18	83	71	50
19	3	2	50
20	21	3	50
8	K	1	
0	367	368	25
1	321	320	55
2	123	120	13
3	214	212	89
4	97	96	96
5	41	41	3
6	67	65	12
7	62	73	2
8	27	30	71
9	68	47	73
10	89	88	93
11	56	52	91
12	58	58	73
13	82	79	50
14	65	73	61
15	142	145	93
16	80	83	84
17	47	42	80
18	25	19	83
19	19	19	23
20	37	37	61
8	K	2	
0	606	620	50
1	60	42	19
2	199	189	40
3	190	193	41
4	126	108	66
5	86	90	91
6	181	173	20
7	123	134	15
8	307	316	2
9	129	135	80
10	230	227	77
11	67	59	58
12	126	138	17
13	166	166	49
14	67	46	75
15	48	47	71
16	96	103	57
17	24	9	96
18	40	32	0
19	16	12	38
8	K	3	
0	280	282	75
1	82	56	45
2	382	371	6
3	190	186	55
4	134	121	21
5	128	128	66
6	40	40	29
7	171	164	51
8	89	95	27
9	128	134	6
10	104	116	72
11	184	180	97
12	121	125	86
13	67	76	78
14	35	27	42
15	39	40	15
16	100	96	21
17	38	29	95
18	64	73	86
19	5	9	36
8	K	4	
0	90	87	0
1	182	180	64
2	151	141	82
3	32	36	73
4	158	149	10
5	177	179	68
6	81	80	24
7	188	183	21
8	53	65	67
9	144	140	13
10	141	145	26
11	112	109	2
12	290	275	69
13	45	50	64
14	135	137	73
15	54	48	78
16	36	34	52
17	42	50	18
18	48	45	51
19	28	32	68
8	K	5	
0	158	181	25
1	120	117	45
2	255	252	65
3	208	210	33
4	347	358	93
5	150	153	37
6	203	204	90
7	98	85	95
8	26	31	99
9	139	130	98
10	115	127	22
11	64	56	38
12	131	128	33
13	102	99	3
14	50	51	10
15	46	45	67
16	43	53	88
17	34	21	51
18	63	61	35
8	K	6	
0	134	124	0
1	97	83	17
2	232	233	41
3	211	228	2
4	81	82	14
5	120	122	26
6	149	145	96
7	172	173	50
8	126	135	30
9	85	82	78
10	74	77	1
11	172	154	93
12	36	32	24
13	148	136	95
14	8	14	17
15	1	5	97
16	23	18	71
17	19	10	66
8	K	7	
0	11	10	75
1	53	59	21
2	120	120	93
3	59	55	82
4	266	271	58
5	175	170	0
6	55	56	26
7	166	177	12
8	34	22	11
9	148	153	52
10	123	117	37
11	63	54	97
12	34	24	90
13	48	43	47
14	1	8	62
15	55	51	49
16	16	14	27
8	K	8	
0	73	89	0
1	73	77	84
2	102	107	15
3	183	189	51
4	96	97	36
5	120	127	38
6	139	135	40
7	17	15	23
8	48	64	7
9	85	69	22
10	58	50	0
11	69	53	51
12	60	46	28
13	28	19	78
14	17	13	26
15	19	11	67
8	K	9	
0	90	92	75
1	70	71	61
2	87	93	17
3	64	65	96
4	170	179	4
5	21	20	18
6	57	53	46
7	46	39	51
8	46	66	28
9	62	68	5
10	72	67	90
11	29	30	58
12	51	46	54
13	12	14	93
8	K	10	
0	97	96	50
1	87	85	29
2	53	54	89
3	40	32	67
4	60	61	79
5	74	72	54
6	59	70	68
7	35	34	72
8	34	33	59
9	56	69	36
10	47	46	37
11	15	8	37
8	K	11	
0	28	33	25
1	41	32	42
2	33	39	66
3	38	41	26
4	25	37	41
5	3	7	34
6	45	38	66
7	40	30	73
8	55	43	45
9	12	3	76
8	K	12	
0	20	24	0
1	18	10	68
2	27	23	30
3	48	41	1
4	61	54	29
9	K	0	
1	12	19	75
2	271	263	25
3	158	154	75
4	27	37	75
5	28	12	25
6	162	168	75
7	70	64	25
8	259	256	75
9	193	194	75
10	95	101	75
11	133	140	25
12	27	32	75
13	40	45	75
14	21	4	75
15	51	37	25
16	59	60	25
17	35	33	25
18	12	10	25
19	20	10	25
9	K	1	
0	452	438	75
1	161	158	47
2	89	81	26
3	143	140	77
4	187	182	29
5	78	86	71
6	79	84	64
7	127	137	55
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7	56	60	79
8	78	71	44
9	34	26	6
10	54	48	83
11	31	29	12
12	35	38	62
13	54	50	96
14	K	4	
0	12	10	50
1	40	30	48
2	80	76	56
3	22	27	40
4	52	44	55
5	65	72	33
6	57	55	91
7	96	94	37
8	54	49	5
9	79	81	78
10	0	11	38
11	30	30	50
12	27	26	64
14	K	5	
0	46	35	25
1	26	24	33
2	8	11	27
3	63	63	65
4	46	48	62
5	50	48	87
6	43	39	64
7	6	12	32
8	27	29	98
9	45	46	60
10	44	42	26
11	56	54	61
14	K	6	
0	15	3	0
1	24	15	53
2	73	76	44
3	87	85	64
4	11	2	18
5	33	28	97
6	37	39	56
7	22	20	7
8	56	56	58
9	57	59	12
10	72	73	4
14	K	7	
0	29	32	75
1	18	16	27
2	50	44	11
3	69	69	48
4	51	50	9
5	20	22	85
6	16	18	24
7	18	23	18
8	27	26	39
14	K	8	
0	37	39	50
1	56	46	90
2	36	40	97
3	23	21	58
4	15	18	100
5	77	71	62
6	17	20	2
15	K	0	
0	9	0	25
1	49	53	75
2	56	65	75
3	8	11	25
4	7	5	25
5	23	23	75
6	44	32	25
7	15	17	25
8	12	8	25
9	57	51	25
10	2	3	25
11	23	17	75
12	33	20	25
15	K	1	
0	42	35	75
1	32	32	76
2	16	10	7
3	63	64	92
4	32	25	80
5	26	19	39
6	47	42	39
7	18	15	69
8	23	19	99
9	17	15	25
10	22	22	82
11	20	17	24
12	36	36	24
15	K	2	
0	20	8	50
1	48	43	33
2	35	39	33
3	6	6	38
4	62	60	88
5	31	29	9
6	40	34	70
7	49	45	22
8	19	22	52
9	32	31	67
10	22	24	23
11	11	3	93
12	8	2	38
15	K	3	
0	38	33	25
1	37	30	98
2	34	35	20
3	60	53	37
4	53	48	35
5	53	52	8
6	25	21	83
7	14	9	86
8	22	18	29
9	0	7	89
10	17	16	86
11	34	30	64
15	K	4	
0	17	10	50
1	45	42	62
2	39	32	52
3	34	45	85
4	31	30	40
5	27	20	67
6	39	35	43
7	36	38	40
8	14	5	29
9	37	35	30
10	42	38	99
15	K	5	
0	24	26	25
1	35	37	40
2	14	17	65
3	36	28	67
4	6	6	4
5	56	57	66
6	41	46	22
7	43	37	11
8	7	6	73
9	28	23	41
15	K	6	
0	71	65	0
1	41	38	3
2	40	42	86
3	33	31	64
4	19	11	43
5	34	22	40
6	45	32	87
7	41	37	75
8	22	20	60
15	K	7	
0	54	56	75
1	25	22	44
2	40	38	3
3	49	40	31
4	35	35	63
5	32	40	23
16	K	0	
0	17	6	50
1	15	7	0
2	28	19	50
3	0	14	0
4	12	20	50
5	14	23	0
6	0	5	50
7	11	19	50
8	42	47	50
9	49	44	0
10	32	34	0
16	K	1	
0	19	15	25
1	26	22	65
2	24	20	94
3	42	35	12
4	29	25	96
5	11	20	84
6	18	21	7
7	30	26	87
8	33	25	60
9	23	22	66
10	27	27	94
16	K	2	
0	16	21	50
1	17	1	27
2	17	6	19
3	69	69	83
4	41	40	92
5	7	9	14
6	18	22	30
7	15	17	80
8	37	28	19
9	8	4	57
10	19	14	26
16	K	3	
0	25	25	25
1	51	43	17
2	38	36	39
3	40	36	56
4	7	5	59
5	17	17	9
6	22	24	73
7	12	18	44
8	37	37	17
9	30	30	32
16	K	4	
0	58	55	0
1	26	17	95
2	24	29	14
3	20	23	35
4	29	31	17
5	23	20	36
6	31	20	72
7	16	13	91
8	21	15	58
16	K	5	
0	21	27	75
1	45	33	44
2	0	9	98
3	37	31	7
4	21	15	72
5	18	18	67
6	17	13	15
16	K	6	
0	54	51	50
1	12	13	18
2	5	16	83
3	39	35	28
4	14	5	2
17	K	0	
0	0	0	26
1	54	49	75
2	5	7	75
3	46	44	75
4	54	48	75
5	20	13	75
6	11	2	25
7	0	4	75
8	9	8	75
17	K	1	
0	18	23	75
1	26	20	72
2	26	16	56
3	10	10	61
4	26	26	24
5	31	32	68
6	42	36	80
7	24	24	30
17	K	2	
0	46	36	0
1	26	13	53
2	40	40	7
3	37	35	1
4	34	33	23
5	11	10	33
6	36	35	91
7	15	14	79
17	K	3	
0	0	2	25
1	21	18	26
2	13	3	34
3	12	19	1
4	4	6	71
5	45	41	13
6	5	7	74
17	K	4	
0	25	19	0
1	46	33	12
2	12	6	90
3	23	25	50
4	14	10	74
18	K	0	
0	39	37	0
1	19	19	50
2	30	29	0
3	35	34	50
18	K	1	
0	38	29	75
1	35	31	96
2	58	44	99
18	K	2	
0	14	0	50

group is a rare occurrence. Acid dimers are usually formed around centers of symmetry, although in trimesic acid (Duchamp & Marsh, 1969), pairs of carboxyl groups are linked by hydrogen bonds around centers of symmetry, twofold axes, and general positions. In the latter two cases in trimesic acid, the carboxyl groups are disordered, and the two C–O distances in each carboxyl group are nearly equal, ranging from 1·24 to 1·28 Å. In levopimaric acid, the four C–O distances range from 1·24 to 1·28 Å [Fig. 2(a)], suggesting that

Table 4. *Coordinates and thermal parameters*† *for levopimaric acid*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0·2880 (4)	0·3919 (3)	0·4187 (5)	7·40	4·73	4·56	0·11	−1·11	−0·79
C(2)	0·3756 (4)	0·3712 (3)	0·3731 (6)	7·19	4·42	6·79	−0·21	−1·62	−0·47
C(3)	0·3716 (4)	0·3012 (3)	0·3129 (5)	7·11	3·98	5·85	0·82	−1·63	−0·26
C(4)	0·3045 (4)	0·3004 (2)	0·2178 (4)	5·88	2·89	4·34	−0·06	0·61	0·15
C(5)	0·2156 (4)	0·3260 (2)	0·2637 (4)	5·71	3·11	4·06	−0·01	−0·06	0·10
C(6)	0·1467 (3)	0·3237 (3)	0·1736 (5)	4·86	3·64	5·58	−0·33	0·00	−1·30
C(7)	0·0584 (4)	0·3363 (3)	0·2257 (6)	5·49	3·92	7·98	−0·80	0·55	−1·82
C(8)	0·0617 (4)	0·4024 (3)	0·2936 (5)	5·35	3·98	5·47	−0·38	0·71	−0·60
C(9)	0·1281 (4)	0·4038 (3)	0·3828 (5)	6·78	3·84	4·58	0·75	0·33	−0·26
C(10)	0·2185 (4)	0·3964 (2)	0·3276 (4)	5·96	2·79	4·35	−0·40	−0·02	0·03
C(11)	0·1163 (5)	0·4652 (3)	0·4651 (5)	9·83	5·99	4·33	2·66	−0·50	−0·60
C(12)	0·0727 (4)	0·5277 (3)	0·4155 (5)	7·55	4·26	4·77	0·63	−0·14	−0·90
C(13)	0·0248 (4)	0·5246 (3)	0·3236 (5)	5·29	4·42	4·97	0·03	0·71	−0·40
C(14)	0·0150 (4)	0·4574 (3)	0·2654 (5)	4·92	4·65	5·07	−0·25	0·46	−0·85
C(15)	0·2939 (4)	0·2243 (3)	0·1836 (5)	5·72	3·78	4·36	0·20	0·47	0·36
C(16)	0·3386 (4)	0·3402 (3)	0·1156 (5)	6·75	3·68	5·36	−0·29	1·16	0·43
C(17)	0·2345 (4)	0·4599 (2)	0·2509 (5)	6·37	2·89	5·17	−0·77	−0·22	0·28
C(18)	−0·0197 (4)	0·5855 (3)	0·2687 (5)	6·86	4·52	5·32	0·47	1·18	0·27
C(19)	−0·0333 (6)	0·6463 (3)	0·3462 (7)	12·50	4·91	7·56	3·26	0·11	0·14
C(20)	0·0305 (5)	0·6076 (3)	0·1648 (5)	8·27	6·80	6·46	−0·53	0·73	1·38
O(1)	0·3207 (3)	0·2038 (2)	0·0908 (3)	10·23	3·68	4·96	−0·08	1·47	−0·37
O(2)	0·2593 (3)	0·1832 (2)	0·2549 (3)	8·80	3·04	4·86	−0·24	1·45	0·39
C(1*)	0·1660 (3)	0·8313 (2)	0·1335 (4)	5·35	4·14	6·79	−0·58	−0·32	−0·10
C(2*)	0·1493 (3)	0·8726 (2)	0·0255 (4)	6·61	5·14	6·84	−0·45	−1·94	−0·52
C(3*)	0·1759 (3)	0·9478 (2)	0·0416 (4)	6·08	4·52	5·67	0·37	−0·91	0·30
C(4*)	0·2703 (3)	0·9548 (2)	0·0744 (3)	5·30	3·45	3·71	0·60	0·55	−0·39
C(5*)	0·2882 (2)	0·9089 (2)	0·1802 (3)	4·74	2·99	3·77	0·01	0·66	−0·14
C(6*)	0·3805 (2)	0·9145 (2)	0·2237 (4)	4·54	3·48	5·80	−0·51	−0·24	0·00
C(7*)	0·3908 (3)	0·8807 (2)	0·3381 (4)	6·52	4·42	5·60	−0·37	−2·08	0·01
C(8*)	0·3576 (3)	0·8078 (2)	0·3332 (4)	6·10	4·22	4·56	0·72	0·02	0·20
C(9*)	0·2664 (3)	0·8024 (2)	0·2925 (4)	5·69	3·15	4·92	−0·17	0·64	0·22
C(10*)	0·2588 (2)	0·8319 (2)	0·1706 (4)	4·70	3·11	4·59	−0·16	0·31	−0·43
C(11*)	0·2287 (3)	0·7276 (2)	0·3094 (4)	6·94	4·04	7·44	−0·53	0·89	1·31
C(12*)	0·2963 (4)	0·6716 (2)	0·3193 (5)	9·87	3·20	9·57	−0·30	2·90	1·12
C(13*)	0·3762 (4)	0·6819 (2)	0·3403 (6)	7·71	4·54	9·90	0·87	3·06	2·29
C(14*)	0·4058 (3)	0·7537 (2)	0·3573 (4)	7·23	4·91	6·64	0·90	0·83	1·27
C(15*)	0·2800 (3)	1·0304 (2)	0·1089 (4)	5·21	3·63	4·41	0·16	0·32	0·42
C(16*)	0·3294 (3)	0·9404 (2)	−0·0242 (4)	8·42	4·70	4·22	0·64	1·83	0·11
C(17*)	0·3130 (3)	0·7869 (2)	0·0902 (4)	6·97	3·26	5·77	0·15	1·18	−0·87
C(18*)	0·4475 (5)	0·6265 (3)	0·3533 (8)	13·89	5·33	20·06	3·99	9·86	4·47
C(19*)	0·4293 (5)	0·5684 (4)	0·4096 (7)	15·21	9·51	10·57	5·60	3·36	2·82
C(20*)	0·5000 (4)	0·6257 (3)	0·2464 (6)	9·57	5·58	10·81	0·79	2·64	−0·76
O(1*)	0·2550 (2)	1·0504 (1)	0·2040 (2)	10·34	3·36	4·82	0·05	2·44	−0·72
O(2*)	0·3102 (3)	1·0724 (1)	0·0379 (3)	11·39	4·00	5·32	−1·08	2·22	0·53

† The thermal parameters are of the form

$$T = \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$
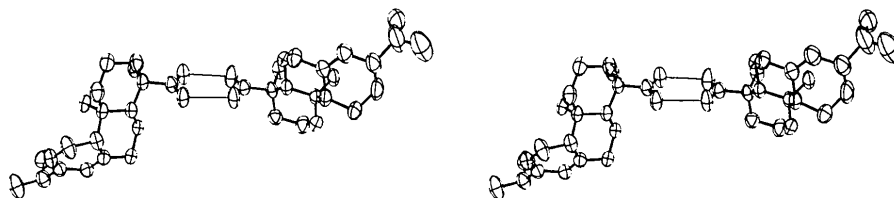
The B_{ij} values are in Å² units.

Fig. 1. Stereodiagram of the dimer of levopimaric acid prepared from a computer program (Johnson, 1965). Molecule *A* is on the left and molecule *B* is on the right of the hydrogen bonds.

these carboxyl groups have a twofold disorder. There was no indication of the positions of the protons in difference maps. The thermal parameters for the oxygen atoms (Table 4) are large only in the direction perpendicular to the planes of the carboxyl groups. Similarly, large out-of-plane displacements for the O atoms were observed in trimesic acid. Other carboxylic acids in which nearly equal C–O distances have been observed are 1,6-methanocyclodecapentaene-2-carboxylic acid (Dobler & Dunitz,1965), fluoromalonic acid (Roelofsen, Kanters, Kroon & Vliegenthart, 1971) and COOH[CH₂]₁₁COOH (Housty, 1968). In each of these three structures, the dimers are formed around centers of symmetry.

Fig. 3. Torsional angles for molecule A (in regular type) and molecule B (in italics). The values in brackets are the deviations (in Å units) from planarity in ring C.

Each of the carboxyl groups in the two molecules of levopimaric acid is planar to within ±0·01 Å, and the two planes are nearly parallel with a dihedral angle of only 2°43'. In dimers formed around a center of symmetry, planes for the two carboxyl groups must be parallel, but not necessarily coplanar. Displacements of as much as 0·5 Å have been observed (Jeffrey & Sax, 1963). In the present investigation, the plane of one carboxyl group is displaced by ~0·2 Å from the other.

A preferred conformation for the carboxyl group, where C_α–C_β is saturated, has been noted (Dunitz & Strickler, 1968). The torsion angle C_β–C_α–$C=0$ has been observed to be near zero. In cyclohexane-1,4-trans-dicarboxylic acid, for example, the C=O bond is synplanar with the C_α–C_β bond in the ring as shown in (I). In levopimaric acid, where three C_β atoms are attached to C_α and where the two C–O bonds are nearly indistinguishable, there appears to be a preference for the carboxyl group to assume the more symmetric conformation (II), with torsional angles C(16)–C(4)–C(15)–O(1) = +7·7° and C(16*)–C(4*)–C(15*)–O(2*) = +20·9°.
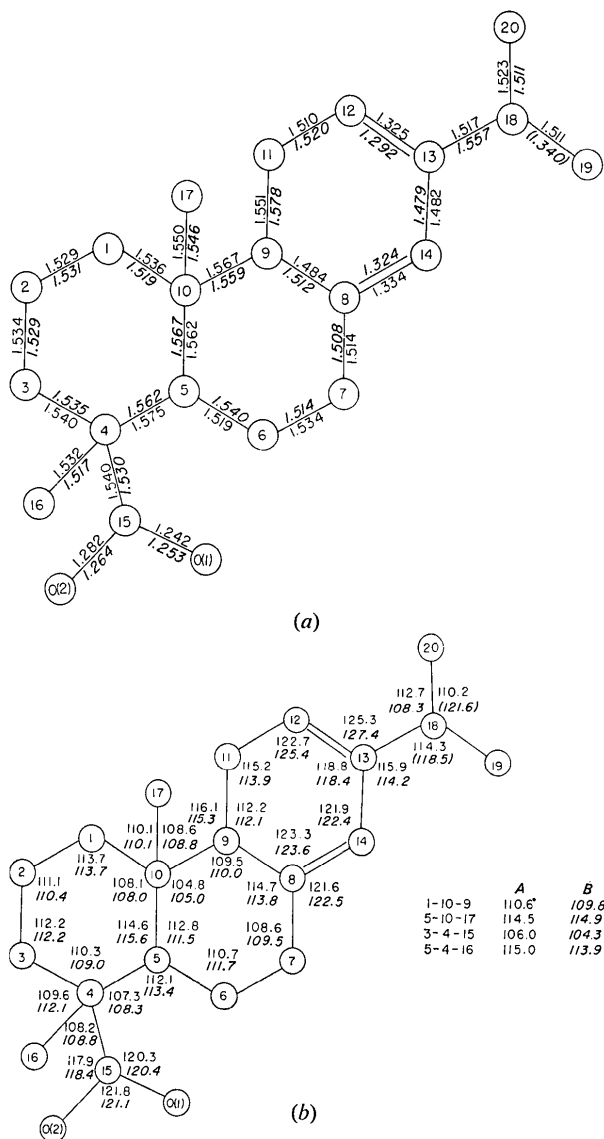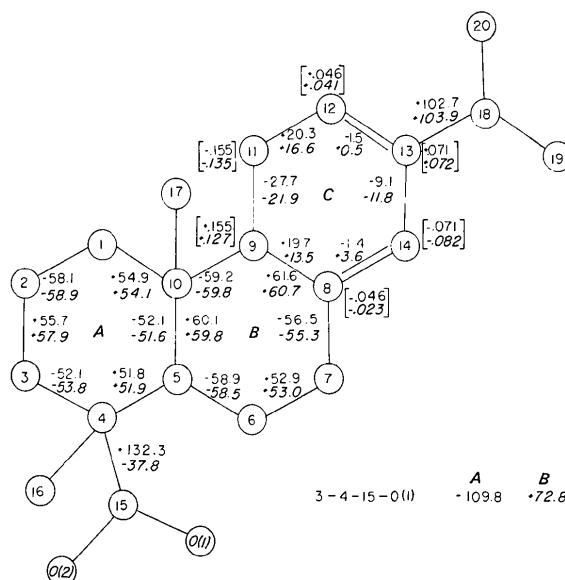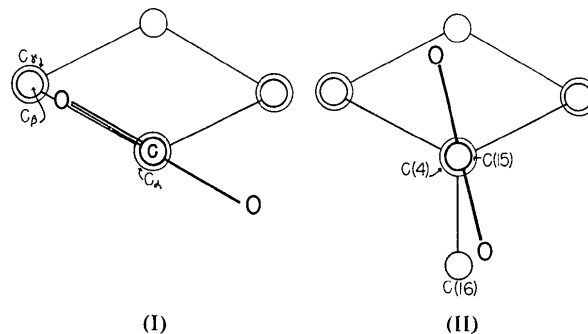

(a)

(b)

Fig. 2.(a) Bond lengths for molecule A (in regular type) and for molecule B (in italics). The standard deviations are 0·008 Å, except for C(18*)–C(19*) in molecule B where it is 0·011 Å. (b) Bond angles. The standard deviations are ~0·65°.

(I)

(II)

Bond lengths and angles are shown in Fig. 2(a) and (b). Standard deviations computed from the least-squares fit alone, without considering other sources of error, are 0·008 Å for C–C bonds, [except for C(18*)–C(19*) in molecule B where the standard deviation is 0·011 Å] and 0·65° for the CCC angles. The values for the bond lengths and angles are quite comparable for the two independent molecules, except for C(18*)–C(19*) and the bond angles around C(18*). Levopimaric acid has an isopropyl group attached to C(13), and molecule A has bond lengths and angles consistent with such a group. In molecule B, the C(18*)–C(19*) length is only 1·340 Å, and angles C(13*)–C(18*)–C(19*) and C(20*)–C(18*)–C(19*) are 118·5° and 121·6°, respectively, which are considerably larger than tetrahedral values. From both the least-squares refinement and Fourier maps, it was apparent that atoms C(18*) and C(19*) have the largest thermal factors, much larger than C(18) and C(19). There does not appear to be any indication of a double bond in this position from nuclear magnetic resonance data taken on material from the same source as the crystal used in the X-ray experiment (Weiss, private communication). It is unlikely that additional refinement of the data would significantly alter the anomalous values around C(18*) and C(19*), since the values for the bond lengths and angles changed very little during the refinement. No absorption correction had been applied to the data. The cross-section of the crystal was 0·5 × 0·7 mm; for $\mu = 5·57$ cm^{-1}, the factors by which the intensities would need to be multiplied would vary from 1·32 to 1·47, a variation of ~5·5% about a mean intensity or less than 3% about a mean $|F_o|$. The lack of absorption correction would primarily affect the thermal factors. A probable source of error which could affect the bond lengths and angles is the large size of the crystal used for data collection. The crystal may not have been uniformly bathed in the X-ray beam, causing systematic errors in the intensities of some reflections.

Rings A and B have the chair conformation. Values for the torsional angles are shown in Fig. 3. They are of the same order of magnitude as values observed for other steroids with rings in the chair conformation (see e.g. Cooper, Norton & Hauptman, 1969; Karle, 1970). In ring A, the CH$_3$ groups on C(4) and C(10) are both axial. For an ideal chair conformation for ring A, the C atoms of these two CH$_3$ groups would be separated by only 2·5 Å. Actually, the C(16)···C(17) distances in the two molecules are 3·26 and 3·28 Å, although H(16–3)···H(17–3) is only ~2·0 Å. This CH$_3$···CH$_3$ repulsion has the effect of increasing the value of the C(4)–C(5)–C(10) angle to ~115° and decreasing the value of the C(5)–C(10)–C(9) angle to ~105°.

Another site of intramolecular crowding is between H(1–1) and H(11–2), the β H atoms on C(1) and D(11), where the separation is only ~2·0 Å. The repulsion between these H atoms appears to have increased the value of the C(10)–C(9)–C(11) angle to 115–116°. In addition, there is a distinct increase in the length of the four C–C bonds between C(4) and C(11), the region of crowding, where the average of the eight values is 1·565 Å as compared to an average length of 1·526 Å for remaining single bonds in rings A and B.

Deviations from planarity in ring C are rather large (Fig. 3). Nevertheless, the five atom groupings around each double bond are planar to within ± 0·013 Å, except in molecule B around the C(8*) = C(14*) bond where four atoms are nearly coplanar and either C(7) or C(13) deviates by 0·14 Å. The diene system is not coplanar but has a twist about the C(13)–C(14) bond of −9·1 and −11·8° in molecules A and B, respectively. The existence of the twist and the direction had been correctly predicted by the negative Cotton effect (Burgstahler et al., 1961).

The folded conformation between rings B and C as postulated from the negative Cotton effect has also been confirmed. The dihedral angle between the least-squares planes through ring B and through ring C is 43·7° for molecule A and 39·9° for molecule B. Rings A and B are also somewhat bowed with respect to each other, the bowing probably being enhanced by the repulsion between the axial CH$_3$ groups on C(4) and C(10). The dihedral angles between the least-squares planes through rings A and B are −8·7 and −9·6° for molecules A and B respectively.

Packing in the crystal is illustrated in Fig. 4. The dominant feature is the formation of dimers from the two independent molecules by hydrogen bonding between the carboxyl groups. There are no other hydrogen bonds. The closest intermolecular approaches are
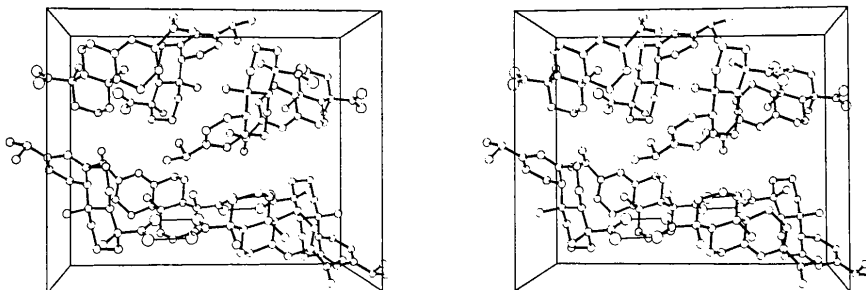

Fig. 4. The contents of a unit cell of levopimaric acid. The axial directions are a↓, b→ and c up from the plane of the page. The larger circles denote O atoms, and hydrogen bonds are represented by the light lines.

between $O(1^*) \cdots C(16^*)$ at 3·49 Å and $C(20) \cdots C(16^*)$ at 3·68 Å. All other $C \cdots C$ distances are greater than 3·75 Å.

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The Crystal Structure of Bismuth (2:1) Borate, 2Bi₂O₃.B₂O₃

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The crystal structure of bismuth (2:1) borate ($2Bi_2O_3.B_2O_3$) was determined by single-crystal X-ray diffraction analysis. Proper classification of this compound is as an oxide-orthoborate with the formula $Bi_4O_3(BO_3)_2$. The material crystallizes in the monoclinic system, $P2_1/c$, with 4 formula units in a cell of dimensions $a = 11\cdot107$, $b = 6\cdot627$, $c = 11\cdot044$ Å and $\beta = 91\cdot04°$. Intensity data were obtained on an automated diffractometer using Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å). Bismuth positions were established by direct phase determining procedures and the remaining atomic positions found from a three-dimensional difference synthesis phased by the bismuth atoms. Full-matrix, least-squares, isotropic refinement of the structure yielded a residual $R = 5\cdot1$ % for 2098 observed reflections. The structure contains discrete planar BO_3^{3-} anions held together by coordination to bismuth atoms. Additional oxygen atoms, coordinated only to bismuth, are present. The average B–O distances is 1·38 Å. The minimum Bi–O distance found is 2·14 Å. Some of the bismuth atoms do not have a clearly delineated coordination shell.

Introduction

The analysis of the structure of bismuth (2:1) borate has been undertaken as part of a general program for the study of borate compounds. In a previous study (Weir & Schroeder, 1964) the infrared spectrum of $2Bi_2O_3.B_2O_3$ was interpreted as indicative of a structure containing an anion which was a complex polymer of trigonal BO_3 groups. An X-ray structure analysis was performed to test this hypothesis.

Experimental

Single crystals of bismuth (2:1) borate were grown from a stoichiometric melt on a hot wire loop. The crystals were ground into spheres in anticipation of