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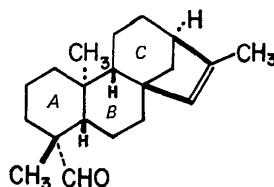
The Structure of (–)-Kaur-15-en-19-al, an Aldehyde Isolated from *Espeltia Weddellii*

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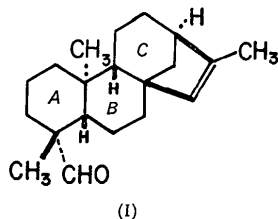
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An aldehyde, $C_{20}H_{30}O$, isolated from the Venezuelan plant *Espeltia weddellii*, has been identified by its crystal structure analysis to be (–)-kaur-15-en-19-al,



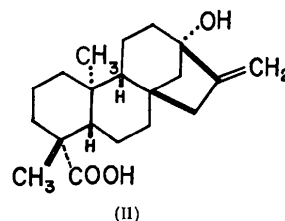
Ring junction *A–B* is *trans* while *B–C* is *cis*. Comparison with related compounds of known absolute configuration indicates that this molecule has a configuration opposite to that of the steroids. The intensities of reflexions decreased rapidly with scattering angle, and there is considerable positional disorder in the cell. The material crystallizes in space group $P2_12_12_1$ with cell dimensions $a = 11.654 \pm 0.005$, $b = 22.644 \pm 0.007$, $c = 6.370 \pm 0.004$ Å and $Z = 4$. The structure was solved by the application of the symbolic addition procedure for the phase determination in noncentrosymmetric space groups.

The original aim of this study was to establish the structural formula of a diterpenoid, whose empirical formula is $C_{20}H_{30}O$, which had been isolated from the tubers of *Espeltia weddellii*, a Composita which grows at 10,000 feet in the Venezuelan Andes. The elucidation of the structure showed the formula to be:



It is identical to the aldehyde extracted from *Espeltia tenore*, also occurring in the Venezuelan Andes (Usubillaga & Morales, 1970). The fungus *Fusarium moniliforme* Sheld also produces a number of diterpenoids closely related to (I) (Serebryakov, Simolin & Kuche-

rov, 1970). These diterpenoids belong to the (–)-kaurane group (see, e.g., Cross, Galt, Hanson, Curtis, Grove & Morrison, 1963; Briggs, Cambie & Rutledge, 1963) and are of particular interest in the biosynthesis of gibberellins (Hanson & White, 1969). They are also related to steviol (II), prepared by the enzymatic hydrolysis of stevioside, whose absolute configuration has been established by chemical means (Mossettig, Beglinger, Dolder, Lichti, Quitt & Waters, 1963). In spite of their superficial resemblance to steroids, the kaurane diterpenoids have the antipodal absolute configuration.



A structural point of interest is the apparent crowding of the C(18) methyl group (Fig. 1) between the aldehyde moiety and atoms C(12) and C(14) of ring C which is *cis* with respect to ring B.

Experimental

Crystals of (-)-kaur-15-en-19-al were obtained by means of ethanolic extraction of the tubers of *Espeletia weddellii* and chromatographic separation. They were prepared and made available to us by Drs A. Usabillaga and A. Morales from the Universidad de Los Andes, Merida, Venezuela. The colorless, lath-shaped crystals adhered to each other very tenaciously. Physical data are given in Table 1. A carefully brushed single crystal was mounted on the *c* axis, and intensity data were collected on a four-circle automatic diffractometer using the θ - 2θ (moving-crystal moving-counter) technique with a $2\cdot0^\circ + 2\theta(\alpha_2) - 2\theta(\alpha_1)$ scan over 2θ . The intensities faded rapidly with scattering angle, and the measurable data are from reflections with $\theta < 45^\circ$. Intensities were corrected for Lorentz and polarization factors, and normalized structure factors $|E|$ were derived.

Table 1. Physical data

| | |
|-----------------------------------|---|
| Molecular formula | C ₂₀ H ₃₀ O |
| M.W. | 286.5 |
| Melting point | 121 °C |
| Habit | Colorless laths |
| Crystal size | 0.04 × 0.08 × 0.6 mm |
| Space group | P2 ₁ 2 ₁ 2 ₁ |
| <i>a</i> | 11.654 ± 0.005 Å |
| <i>b</i> | 22.644 ± 0.007 |
| <i>c</i> | 6.370 ± 0.004 |
| <i>V</i> | 1681 Å ³ |
| <i>Z</i> | 4 molecules per unit cell |
| Density (calc) | 1.132 g.cm ⁻³ |
| Radiation | Cu Kα (Ni filter) |
| Wave length | 1.5418 Å |
| Number of independent reflections | 765 |

Phases were obtained directly from the magnitudes of the normalized structure factors $|E|$ by means of the symbolic addition procedure for noncentrosymmetric crystals (Karle & Karle, 1966). Table 2 lists the assignment of phase values made to reflections with high $|E|$ values in order to specify the origin, choose the enantiomorph, and implement the sum-of-angles formula:

$$\phi_h \simeq \langle \phi_k + \phi_{h-k} \rangle_{kr} \quad (1)$$

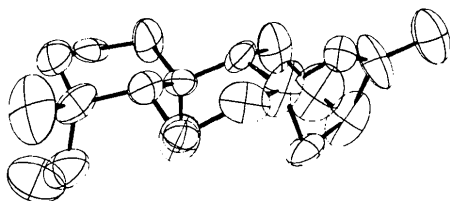


Fig. 2. Stereodiagram of the molecule (Johnson, 1965). Thermal ellipsoids are at the 50% probability level.

Phases for 45 additional reflections with large $|E|$ were derived from the assignments in Table 2. From multiple indications, it was apparent that $a = \pi$, $b = 0$ and $c = b + \pi/2 = +\pi/2$. Phase values based on the above assignments for symbols *a*, *b*, and *c* were refined, and phases for additional reflections with $|E| > 1.0$ were obtained by means of the tangent formula (Karle & Hauptman, 1956). An *E* map, computed with 238 reflections, contained 11 strong peaks comprising ring B and parts of rings A and C. The remaining atoms were found using a recycling procedure based on the partial structure (Karle, 1968). The recycling procedure had to be repeated several times, since the limited data and the corresponding large values for the thermal parameters, especially for the peripheral atoms in the molecule, did not define the missing atoms very well.

Table 2. Assignment of phase values

| <i>h</i> | ϕ_h | $ E_h $ | |
|----------|-------------------------|---------|----------------|
| 8 7 0 | 0 | 2.56 | } origin |
| 1 18 0 | $+\pi/2^*$ | 3.36 | |
| 0 17 1 | $+\pi/2^*$ | 1.94 | |
| 9 8 1 | $+\pi/4$ | 2.02 | } enantiomorph |
| 6 0 0 | <i>a</i> (0 or π) | 4.00 | |
| 8 8 0 | <i>b</i> (0 or π) | 3.81 | |
| 1 0 5 | <i>c</i> ($\pm\pi/2$) | 2.96 | |

* These values are shown as $-\pi/2$ in Table 3, since an arbitrary shift to a new origin was made after the structure was determined.

A full-matrix least-squares refinement of the coordinates and thermal parameters was performed using program *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 0.5$ for $F_o = 0$, $w = 1$ for $|F_o| < 12$, and $w = \frac{12}{|F_o|}$ for $|F_o| > 12$. Scattering factors listed in *International Tables for X-*

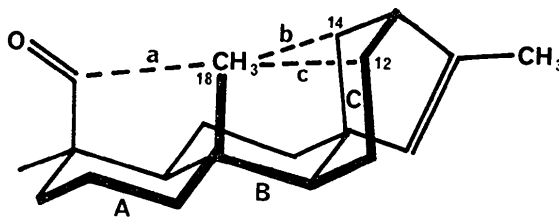


Fig. 1. Close intramolecular approaches in an idealized model. Actually, distances *a*, *b*, and *c* are all greater than 3.0 Å.

Ray Crystallography (1962) were used. A difference map was quite featureless; hence, coordinates for the 30 hydrogen atoms were assumed and introduced as constant parameters in the least-squares refinement. The final *R* value was 11.6%. Observed and calculated structure factors are listed in Table 3.

Discussion

The stereodiagram of the molecule (Fig. 2) displays graphically the large thermal factors, which are listed in Table 4. An examination of the packing in the crystal (Fig. 3) shows large spaces between the molecules. The nearest intermolecular approaches are C(17)···O,

C(6)···O, C(3)···O, and C(5)···O at 3.73, 3.74, 3.75, and 3.81 Å, respectively, and C(3)···C(7) and C(2)···C(20) at 3.84 and 3.91 Å respectively. All other C···C distances are greater than 4.0 Å. These values are much larger than van der Waals separations, and the question arises as to the nature of the intermolecular forces. Kitaigorodsky (1955) discusses this problem with reference to globular hydrocarbons which, for the most part, have rotational disorder, or in some cases appear to be 'freely' rotating in the crystal. Adamantane, C₁₀H₁₆, a highly symmetric molecule, is either ordered in space group *F43m* (Nowacki, 1945) or has a twofold disorder, space group *Fm3m* (Nordman & Schmitkons, 1965). The closest intermolecular C···C approach in

Table 3. Observed and calculated structure factors
Columns represent index *k*, 10|*F*_o|, 10|*F*_c|, and the phase in cycles (×100).

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|----|-----|-----|----|----|-----|-----|-----|-----|-----|-----|----|-----|-----|-----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|-----|----|-----|-----|-----|-----|-----|-----|-----|----|----|----|-----|-----|-----|----|----|-----|-----|-----|-----|----|
| 0 | K | 0 | 10 | 80 | 01 | 0 | 7 | 92 | 104 | 67 | 12 | 62 | 95 | 50 | 2 | K | 4 | 9 | 243 | 207 | 50 | 1 | 262 | 270 | 03 | 0 | 0 | 27 | 75 | 11 | 75 | 84 | 88 | 13 | 102 | 92 | 64 | 7 | 61 | 84 | 31 | 8 | K | 3 | | | | | | | |
| 2 | 109 | 124 | 0 | 0 | 2 | 25 | 8 | 495 | 359 | 39 | 13 | 220 | 187 | 0 | 0 | 30 | 68 | 50 | 10 | 143 | 174 | 61 | 2 | 370 | 332 | 62 | 5 | 4 | 0 | 12 | 66 | 59 | 66 | 14 | 84 | 75 | 51 | 0 | 0 | 24 | 25 | 0 | 0 | 24 | 25 | | | | | | |
| 4 | 410 | 843 | 0 | 0 | 9 | 9 | 184 | 191 | 16 | 14 | 95 | 39 | 80 | 0 | 0 | 71 | 91 | 75 | 11 | 159 | 291 | 37 | 1 | 445 | 434 | 75 | 13 | 0 | 32 | 37 | 13 | 80 | 77 | 65 | 13 | 80 | 77 | 65 | 9 | 24 | 21 | 13 | 1 | 71 | 68 | 98 | | | | | |
| 6 | 102 | 327 | 50 | 0 | 296 | 248 | 0 | 10 | 110 | 110 | 8 | 15 | 59 | 47 | 50 | 0 | 121 | 97 | 75 | 12 | 110 | 109 | 32 | 4 | 221 | 259 | 73 | 2 | 0 | 15 | 14 | 171 | 134 | 72 | 0 | K | J | 10 | 68 | 57 | 80 | 2 | 0 | 14 | 45 | | | | | | |
| 8 | 414 | 402 | 0 | 1 | 70 | 74 | 75 | 11 | 177 | 160 | 37 | 16 | 173 | 139 | 50 | 3 | 36 | 25 | 14 | 13 | 89 | 79 | 33 | 9 | 104 | 93 | 88 | 3 | 416 | 370 | 75 | 5 | K | 4 | 3 | 416 | 370 | 75 | 5 | K | 4 | 11 | 161 | 156 | 87 | 3 | 118 | 176 | 20 | | |
| 10 | 209 | 227 | 50 | 2 | 103 | 127 | 38 | 12 | 79 | 73 | 38 | 4 | 45 | 17 | 74 | 0 | 119 | 107 | 71 | 17 | 9 | 11 | 14 | 0 | 41 | 154 | 75 | 5 | 136 | 139 | 75 | 1 | 57 | 33 | 49 | 2 | 110 | 104 | 72 | 4 | 72 | 87 | 74 | 5 | 0 | 28 | 40 | | | | |
| 12 | 25 | 22 | 50 | 3 | 0 | 25 | 13 | 82 | 87 | 16 | 10 | 0 | 50 | 50 | 0 | 0 | 112 | 109 | 74 | 15 | 36 | 71 | 75 | 7 | 228 | 237 | 19 | 5 | 136 | 139 | 75 | 1 | 57 | 33 | 49 | 2 | 110 | 104 | 72 | 15 | 0 | 1 | 48 | 5 | 0 | 28 | 40 | | | | |
| 14 | 386 | 384 | 50 | 4 | 46 | 48 | 50 | 14 | 41 | 19 | 44 | 19 | 0 | 59 | 50 | 9 | 125 | 107 | 29 | 16 | 16 | 47 | 90 | 8 | 195 | 172 | 84 | 6 | 64 | 52 | 25 | 2 | 118 | 133 | 63 | 3 | 159 | 185 | 8 | 7 | K | 1 | 6 | 37 | 43 | 50 | | | | | |
| 16 | 70 | 53 | 0 | 5 | 8 | 27 | 22 | 19 | 80 | 69 | 74 | 20 | 120 | 114 | 50 | 0 | 130 | 113 | 63 | 17 | 5 | 60 | 48 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | | | |
| 18 | 241 | 256 | 50 | 6 | 37 | 61 | 50 | 10 | 123 | 128 | 75 | 2 | K | 1 | 8 | 0 | 70 | 80 | 16 | 8 | 0 | 8 | 5 | 10 | 101 | 151 | 37 | 8 | 9 | 8 | 25 | 5 | 10 | 151 | 37 | 8 | 9 | 8 | 25 | 5 | 10 | 151 | 37 | 8 | 9 | 8 | 25 | | | | |
| 20 | 180 | 181 | 50 | 7 | 129 | 135 | 75 | 17 | 125 | 121 | 80 | 0 | 002 | 795 | 75 | 0 | 74 | 16 | 0 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 |
| 0 | K | 0 | 10 | 80 | 01 | 0 | 7 | 92 | 104 | 67 | 12 | 62 | 95 | 50 | 2 | K | 4 | 9 | 243 | 207 | 50 | 1 | 262 | 270 | 03 | 0 | 0 | 27 | 75 | 11 | 75 | 84 | 88 | 13 | 102 | 92 | 64 | 7 | 61 | 84 | 31 | 8 | K | 3 | | | | | | | |
| 2 | 109 | 124 | 0 | 0 | 2 | 25 | 8 | 495 | 359 | 39 | 13 | 220 | 187 | 0 | 0 | 30 | 68 | 50 | 10 | 143 | 174 | 61 | 2 | 370 | 332 | 62 | 5 | 4 | 0 | 12 | 66 | 59 | 66 | 14 | 84 | 75 | 51 | 0 | 0 | 24 | 25 | 0 | 0 | 24 | 25 | | | | | | |
| 4 | 410 | 843 | 0 | 0 | 9 | 9 | 184 | 191 | 16 | 14 | 95 | 39 | 80 | 0 | 0 | 71 | 91 | 75 | 11 | 159 | 291 | 37 | 1 | 445 | 434 | 75 | 13 | 0 | 32 | 37 | 13 | 80 | 77 | 65 | 13 | 80 | 77 | 65 | 9 | 24 | 21 | 13 | 1 | 71 | 68 | 98 | | | | | |
| 6 | 102 | 327 | 50 | 0 | 296 | 248 | 0 | 10 | 110 | 110 | 8 | 15 | 59 | 47 | 50 | 0 | 121 | 97 | 75 | 12 | 110 | 109 | 32 | 4 | 221 | 259 | 73 | 2 | 0 | 15 | 14 | 171 | 134 | 72 | 0 | K | J | 10 | 68 | 57 | 80 | 2 | 0 | 14 | 45 | | | | | | |
| 8 | 414 | 402 | 0 | 1 | 70 | 74 | 75 | 11 | 177 | 160 | 37 | 16 | 173 | 139 | 50 | 3 | 36 | 25 | 14 | 13 | 89 | 79 | 33 | 9 | 104 | 93 | 88 | 3 | 416 | 370 | 75 | 5 | K | 4 | 3 | 416 | 370 | 75 | 5 | K | 4 | 11 | 161 | 156 | 87 | 3 | 118 | 176 | 20 | | |
| 10 | 209 | 227 | 50 | 2 | 103 | 127 | 38 | 12 | 79 | 73 | 38 | 4 | 45 | 17 | 74 | 0 | 119 | 107 | 71 | 17 | 9 | 11 | 14 | 0 | 41 | 154 | 75 | 5 | 136 | 139 | 75 | 1 | 57 | 33 | 49 | 2 | 110 | 104 | 72 | 4 | 72 | 87 | 74 | 5 | 0 | 28 | 40 | | | | |
| 12 | 25 | 22 | 50 | 3 | 0 | 25 | 13 | 82 | 87 | 16 | 10 | 0 | 50 | 50 | 0 | 0 | 112 | 109 | 74 | 15 | 36 | 71 | 75 | 7 | 228 | 237 | 19 | 5 | 136 | 139 | 75 | 1 | 57 | 33 | 49 | 2 | 110 | 104 | 72 | 15 | 0 | 1 | 48 | 5 | 0 | 28 | 40 | | | | |
| 14 | 386 | 384 | 50 | 4 | 46 | 48 | 50 | 14 | 41 | 19 | 44 | 19 | 0 | 59 | 50 | 9 | 125 | 107 | 29 | 16 | 16 | 47 | 90 | 8 | 195 | 172 | 84 | 6 | 64 | 52 | 25 | 2 | 118 | 133 | 63 | 3 | 159 | 185 | 8 | 7 | K | 1 | 6 | 37 | 43 | 50 | | | | | |
| 16 | 70 | 53 | 0 | 5 | 8 | 27 | 22 | 19 | 80 | 69 | 74 | 20 | 120 | 114 | 50 | 0 | 130 | 113 | 63 | 17 | 5 | 60 | 48 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | | | |
| 18 | 241 | 256 | 50 | 6 | 37 | 61 | 50 | 10 | 123 | 128 | 75 | 2 | K | 1 | 8 | 0 | 70 | 80 | 16 | 8 | 0 | 8 | 5 | 10 | 101 | 151 | 37 | 8 | 9 | 8 | 25 | 5 | 10 | 151 | 37 | 8 | 9 | 8 | 25 | 5 | 10 | 151 | 37 | 8 | 9 | 8 | 25 | | | | |
| 20 | 180 | 181 | 50 | 7 | 129 | 135 | 75 | 17 | 125 | 121 | 80 | 0 | 002 | 795 | 75 | 0 | 74 | 16 | 0 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 |
| 0 | K | 0 | 10 | 80 | 01 | 0 | 7 | 92 | 104 | 67 | 12 | 62 | 95 | 50 | 2 | K | 4 | 9 | 243 | 207 | 50 | 1 | 262 | 270 | 03 | 0 | 0 | 27 | 75 | 11 | 75 | 84 | 88 | 13 | 102 | 92 | 64 | 7 | 61 | 84 | 31 | 8 | K | 3 | | | | | | | |
| 2 | 109 | 124 | 0 | 0 | 2 | 25 | 8 | 495 | 359 | 39 | 13 | 220 | 187 | 0 | 0 | 30 | 68 | 50 | 10 | 143 | 174 | 61 | 2 | 370 | 332 | 62 | 5 | 4 | 0 | 12 | 66 | 59 | 66 | 14 | 84 | 75 | 51 | 0 | 0 | 24 | 25 | 0 | 0 | 24 | 25 | | | | | | |
| 4 | 410 | 843 | 0 | 0 | 9 | 9 | 184 | 191 | 16 | 14 | 95 | 39 | 80 | 0 | 0 | 71 | 91 | 75 | 11 | 159 | 291 | 37 | 1 | 445 | 434 | 75 | 13 | 0 | 32 | 37 | 13 | 80 | 77 | 65 | 13 | 80 | 77 | 65 | 9 | 24 | 21 | 13 | 1 | 71 | 68 | 98 | | | | | |
| 6 | 102 | 327 | 50 | 0 | 296 | 248 | 0 | 10 | 110 | 110 | 8 | 15 | 59 | 47 | 50 | 0 | 121 | 97 | 75 | 12 | 110 | 109 | 32 | 4 | 221 | 259 | 73 | 2 | 0 | 15 | 14 | 171 | 134 | 72 | 0 | K | J | 10 | 68 | 57 | 80 | 2 | 0 | 14 | 45 | | | | | | |
| 8 | 414 | 402 | 0 | 1 | 70 | 74 | 75 | 11 | 177 | 160 | 37 | 16 | 173 | 139 | 50 | 3 | 36 | 25 | 14 | 13 | 89 | 79 | 33 | 9 | 104 | 93 | 88 | 3 | 416 | 370 | 75 | 5 | K | 4 | 3 | 416 | 370 | 75 | 5 | K | 4 | 11 | 161 | 156 | 87 | 3 | 118 | 176 | 20 | | |
| 10 | 209 | 227 | 50 | 2 | 103 | 127 | 38 | 12 | 79 | 73 | 38 | 4 | 45 | 17 | 74 | 0 | 119 | 107 | 71 | 17 | 9 | 11 | 14 | 0 | 41 | 154 | 75 | 5 | 136 | 139 | 75 | 1 | 57 | 33 | 49 | 2 | 110 | 104 | 72 | 4 | 72 | 87 | 74 | 5 | 0 | 28 | 40 | | | | |
| 12 | 25 | 22 | 50 | 3 | 0 | 25 | 13 | 82 | 87 | 16 | 10 | 0 | 50 | 50 | 0 | 0 | 112 | 109 | 74 | 15 | 36 | 71 | 75 | 7 | 228 | 237 | 19 | 5 | 136 | 139 | 75 | 1 | 57 | 33 | 49 | 2 | 110 | 104 | 72 | 15 | 0 | 1 | 48 | 5 | 0 | 28 | 40 | | | | |
| 14 | 386 | 384 | 50 | 4 | 46 | 48 | 50 | 14 | 41 | 19 | 44 | 19 | 0 | 59 | 50 | 9 | 125 | 107 | 29 | 16 | 16 | 47 | 90 | 8 | 195 | 172 | 84 | 6 | 64 | 52 | 25 | 2 | 118 | 133 | 63 | 3 | 159 | 185 | 8 | 7 | K | 1 | 6 | 37 | 43 | 50 | | | | | |
| 16 | 70 | 53 | 0 | 5 | 8 | 27 | 22 | 19 | 80 | 69 | 74 | 20 | 120 | 114 | 50 | 0 | 130 | 113 | 63 | 17 | 5 | 60 | 48 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | 52 | 36 | 83 | 9 | | | |
| 18 | 241 | 256 | 50 | 6 | 37 | 61 | 50 | 10 | 123 | 128 | 75 | 2 | K | 1 | 8 | 0 | 70 | 80 | 16 | 8 | 0 | 8 | 5 | 10 | 101 | 151 | 37 | 8 | 9 | 8 | 25 | 5 | 10 | 151 | 37 | 8 | 9 | 8 | 25 | 5 | 10 | 151 | 37 | 8 | 9 | 8 | 25 | | | | |
| 20 | 180 | 181 | 50 | 7 | 129 | 135 | 75 | 17 | 125 | 121 | 80 | 0 | 002 | 795 | 75 | 0 | 74 | 16 | 0 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 | 3 | K | 1 | 11 | 162 | 172 | 37 |
| 0 | K | 0 | 10 | 80 | 01 | 0 | 7 | 92 | 104 | 67 | 12 | 62 | 95 | 50 | 2 | K | 4 | 9 | 243 | 207 | 50 | 1 | 262 | 270 | 03 | 0 | 0 | 27 | 75 | 11 | 75 | 84 | 88 | 13 | 102 | 92 | 64 | 7 | 61 | 84 | 31 | 8 | K | 3 | | | | | | | |
| 2 | 109 | 124 | 0 | 0 | 2 | 25 | 8 | 495 | 359 | 39 | 13 | 220 | 187 | 0 | 0 | 30 | 68 | 50 | 10 | 143 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

adamantane is 4.15 Å; however, intermolecular H...H separations are calculated to be of the order of 2.34 Å, which is a normal van der Waals value, and presumably, the interactions between the hydrogen atoms of adjacent molecules hold the crystal together.

The present molecule can be described as an ellipsoid covered with hydrogen atoms, with the exception of the aldehyde group. If calculated positions of the H atoms are used (assuming C-H distances near 1 Å and tetrahedral angles) there are nine intermolecular H...H contacts between 2.17 and 2.5 Å, which could act as attractive forces. It is not surprising, however, that the molecules are not held rigidly and that they appear to have positional disorder.

An idealized model of the molecule with tetrahedral angles would have intramolecular distances to C(18), designated as *a*, *b*, and *c* in Fig. 1, near 2.5 Å. Actually the bond angles and torsional angles in rings *A*, *B*, and *C* deviate enough from idealized values so that distances *a*, *b*, and *c* are all greater than 3.0 Å. Torsional angles for rings *A*, *B*, and *C*, shown in Fig. 4, deviate both above and below the ideal value of 60° for a chair conformation. Ring *C* is especially distorted, since atoms C(8), C(13) and C(14) are also members of a 5-membered ring. The two parameters that probably account the most for the increase in the C(18)...C(20) distance are the C(5)-C(10)-C(18) and C(5)-C(4)-C(20) angles, both near 114-115°. In a similar circumstance in *levo*-pimaric acid, one of the components of rosin, the distance between methyl groups on C(4) and C(10)

of ring *A* is increased to >3.0 Å by an increase in the value of the same two angles to 114-115° (Karle, 1972).

An examination of the bond lengths in Fig. 5 shows that the positional disorder in the molecule leads to fairly high deviations from 1.53-1.54 Å for C-C single bonds. The standard deviations for the bond lengths range from 0.03 to 0.04 Å and for the angles they are near 1.7°. Two especially large differences from single bond C-C values occur in the C(12)-C(13) and C(13)-C(16) distances, which are 1.35 and 1.70 Å. Another unusual distance is the intramolecular C(11)...C(16) of only 2.80 Å. Refining of assumed coordinates for C(13), changed in order to make more favorable values for the C(12)-C(13) and C(13)-C(16) bonds, merely returned them to the original values. If the crystal were undergoing a solid-state reaction during exposure to

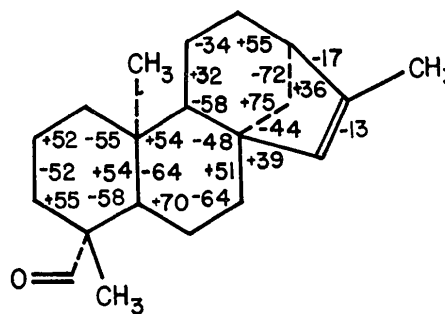


Fig. 4. Torsional angles.

Table 4. Fractional coordinates ($\times 10^4$) and thermal parameters

Thermal parameters are of the form:

$$T = \exp \left[-\frac{1}{3}(B_{11}h^2a^*2 + B_{22}k^2b^*2 + B_{33}l^2c^*2 + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*) \right]$$

B_{ij} values are in Å² units.

| | <i>x</i> | <i>y</i> | <i>z</i> | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| C(1) | 2507 | 1365 | 6737 | 3.07 | 7.34 | 11.49 | 1.33 | -0.28 | -3.59 |
| C(2) | 2000 | 1876 | 7687 | 6.74 | 12.59 | 3.45 | 6.32 | -1.77 | -3.48 |
| C(3) | 2768 | 2440 | 7226 | 11.42 | 6.00 | 4.46 | 2.53 | -0.82 | 0.85 |
| C(4) | 3972 | 2379 | 7763 | 2.88 | 8.02 | 8.10 | 1.76 | -0.47 | 1.30 |
| C(5) | 4460 | 1818 | 6619 | 7.13 | 4.77 | 6.36 | 0.66 | -2.66 | -0.27 |
| C(6) | 5758 | 1716 | 7046 | 4.70 | 5.06 | 10.06 | -1.12 | -0.26 | 0.51 |
| C(7) | 6141 | 1265 | 5326 | 4.09 | 7.31 | 4.72 | -2.99 | 1.34 | 1.32 |
| C(8) | 5558 | 649 | 5508 | 1.20 | 6.32 | 17.13 | -1.15 | -0.63 | 0.26 |
| C(9) | 4225 | 756 | 5654 | 4.66 | 4.28 | 5.85 | 1.07 | -1.30 | 1.06 |
| C(10) | 3773 | 1230 | 7214 | 4.29 | 5.22 | 4.07 | -0.23 | -1.14 | -0.17 |
| C(11) | 3624 | 127 | 5891 | 3.31 | 7.98 | 13.15 | -0.99 | 2.40 | -2.91 |
| C(12) | 4341 | -336 | 7105 | 8.93 | 7.35 | 24.44 | -5.18 | -3.36 | 0.58 |
| C(13) | 5496 | -326 | 6927 | 5.53 | 4.49 | 16.57 | -2.01 | 0.50 | 3.95 |
| C(14) | 5989 | 315 | 7516 | 5.37 | 8.29 | 3.14 | 2.35 | 0.14 | 2.10 |
| C(15) | 5851 | 235 | 3849 | 5.08 | 5.22 | 5.42 | 0.86 | -0.36 | -0.65 |
| C(16) | 5701 | -307 | 4291 | 10.38 | 5.35 | 5.54 | -1.55 | 5.99 | -0.93 |
| C(17) | 5814 | -859 | 3147 | 8.52 | 6.19 | 10.58 | -1.64 | 2.86 | -3.17 |
| C(18) | 3838 | 1073 | 9502 | 5.23 | 6.02 | 8.07 | -0.41 | -2.42 | -0.75 |
| C(19) | 4638 | 2942 | 7127 | 14.67 | 5.36 | 9.55 | -1.82 | 5.39 | 2.99 |
| C(20) | 4195 | 2395 | 10165 | 8.60 | 6.18 | 9.98 | -1.49 | -3.26 | 2.76 |
| O(21) | 3501 | 2534 | 11495 | 14.71 | 15.41 | 5.42 | -0.57 | 0.97 | -1.46 |

Standard deviations ($\times 10^4$)

| | | | |
|-------|----|----|----|
| C(12) | 24 | 10 | 66 |
|-------|----|----|----|

All other atoms:

| | | | |
|--|----|---|----|
| | 15 | 8 | 36 |
|--|----|---|----|

X-rays, then presumably the data collected at the beginning of the experiment would be more representative of the original material. A refinement of half the data collected first reduced the R value several per cent; nevertheless, bond lengths were almost identical with those from the refinement using all available data. As

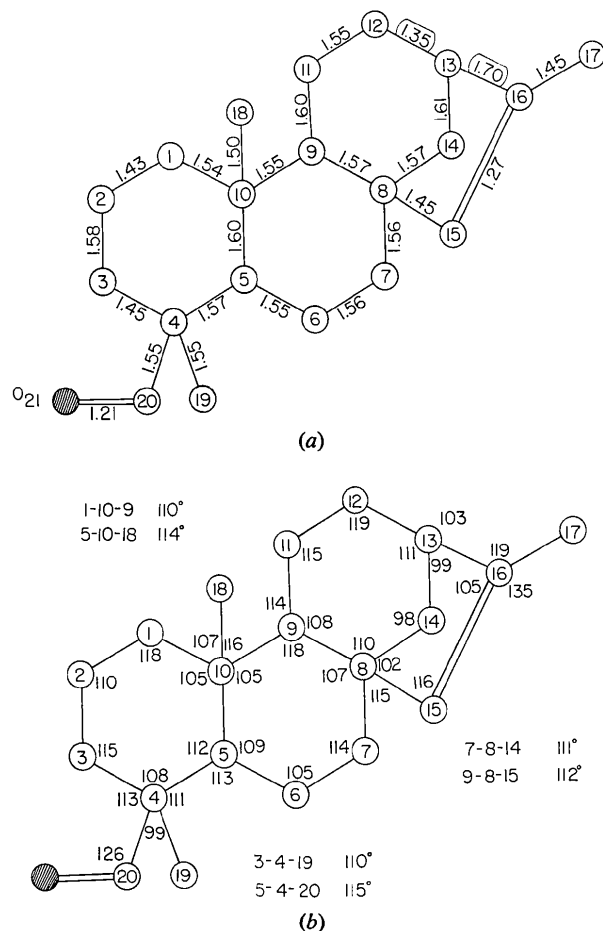


Fig. 5. (a) Bond lengths (standard deviations range from 0.03 to 0.04 Å). (b) Bond angles (standard deviations are about 1.7°).

a further check on the possibility of a solid-state reaction upon exposure to X-rays, some freshly prepared material has been exposed to ultraviolet light in solution, and the new products are being isolated for further examination.

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