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The Crystal and Molecular Structure of a Spiro Triterpane Extracted from Crude Petroleum

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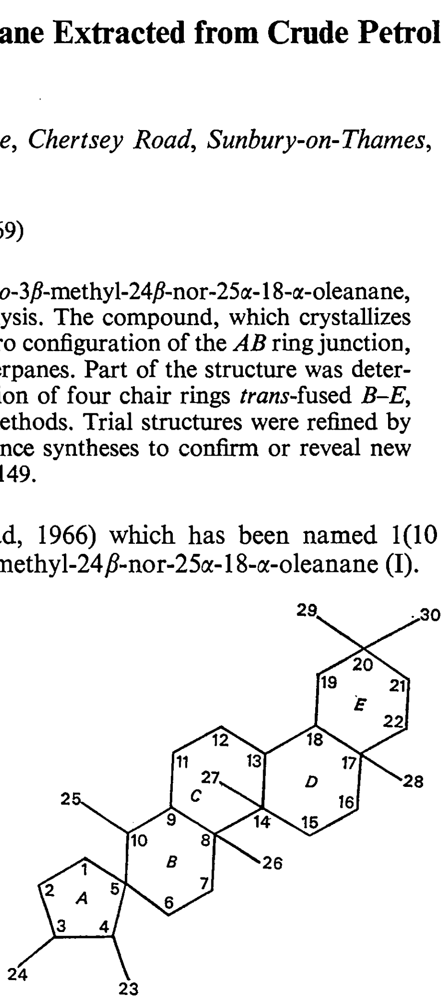
The crystal and molecular structure of the triterpane 1(10→5)-*abeo*-3β-methyl-24β-nor-25α-18-α-oleanane, $C_{30}H_{52}$, has been determined by three-dimensional X-ray analysis. The compound, which crystallizes in the monoclinic system, space group $C2$, possesses a novel spiro configuration of the *AB* ring junction, a feature not hitherto found in known naturally occurring triterpanes. Part of the structure was determined from a Patterson synthesis, which revealed the orientation of four chair rings *trans*-fused *B–E*, and the rest of the molecule was deduced by trial and error methods. Trial structures were refined by least-squares structure factors followed by Fourier and difference syntheses to confirm or reveal new atomic sites. The final *R* index for the carbon atoms only is 0·149.

Introduction

It is commonly held by petroleum chemists and geologists that at least part of crude petroleum has a biological origin. Support for this theory is provided by the optical activity which has been observed in certain petroleum distillates. Hills & Whitehead (1966) have reported upon distillates, boiling in the range 340–550°C, from a number of crude oils with a particular emphasis on a Nigerian crude oil.

From their work they have shown by gas–liquid chromatography, high resolution mass spectrometry and nuclear magnetic resonance spectrometry that crude oils from different sources contain hydrocarbons belonging to the pentacyclic triterpane series C_nH_{2n-8}. Further work on several of the isolated compounds has shown them to be optically active and therefore they must contribute to the observed optical activity in the distillates.

Five compounds of sufficient purity and quantity for comparative examination with known triterpanes have been isolated from a Nigerian crude oil, and the results indicate that they are all skeletally related to naturally occurring triterpenoids through steps which involve removal of the oxygen-containing functional groups, acid isomerization and hydrogenation. All the compounds are fully saturated and as only small (milligram) quantities have been isolated, the introduction of a heavy atom either chemically into the molecule or by co-crystallization with a heavy atom solvent has not been attempted. However the positive identification of the molecular structure of these compounds could be useful in the greater understanding of the origin and formation of crude petroleum. To this end the structure determinations of these compounds have been attempted; of the five compounds so far isolated, the molecular structures of three have been determined. The determination of the remaining two is also being undertaken. This paper describes the structure of one of them, that labelled *E* (Hills & Whitehead, 1966) which has been named 1(10 → 5)-*abeo*-3β-methyl-24β-nor-25α-18-α-oleanane (I).



(I)

Crystal data

Triterpane *E* crystallizes in the monoclinic system as thin transparent plates with the plate face (001), and with principal edges parallel to the *b* axis and [1$\bar{1}$0]. The optic sign is positive as determined from an interference figure on the (001). The crystal density was obtained by flotation in aqueous potassium iodide solution. The cell constants were calculated by extrapolation of successive orders of the principal rows from zero-layer Weissenberg photographs about the principal axes using Cu $K\alpha$ and Cr $K\alpha$ radiations.

Triterpane *E*, $C_{30}H_{52}$, M.W. 412·407 (C=12), m.p. 260°C.

Monoclinic, space group $C2$, absences hkl for $h+k$ odd.

$$a = 11{\cdot}055 \pm 0{\cdot}005\ \text{Å}$$
$$b = 7{\cdot}766 \pm 0{\cdot}005\ \text{Å}$$
$$c = 30{\cdot}03\ \pm 0{\cdot}01\ \text{Å}$$
$$\beta = 96°\ 44' \pm 5'$$
$$U = 2560{\cdot}4\ \text{Å}^3$$
$$D_m = 1{\cdot}066\ \text{g.cm}^{-3}$$

$D_x = 1{\cdot}070$ g.cm^{-3}
$Z = 4$
μ (Cu $K\alpha$) $= 5{\cdot}1$ cm^{-1}
$F(000) = 928$

Optical data

The plate face of the crystal gave an interference figure with the positive acute bisectrix nearly perpendicular to it. The intermediate refractive index β was measured and another index α' close to the lower index α. The shape of the crystal prevented a measurement of γ. The interaxial angle $2V$ was also measured on a universal stage. The values obtained using the mean NaD line are

$$\alpha' = 1{\cdot}559 \pm 0{\cdot}001$$
$$\beta = 1{\cdot}567 \pm 0{\cdot}001$$

and $2V = 54{\cdot}3° \pm 0{\cdot}1°$ corrected for the refractive index of the glass hemisphere.

Experimental

The intensity data were recorded from a crystal of approximate dimensions $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}01$ mm on multiple-film equi-inclination Weissenberg photographs, about the b axis. Using Cu $K\alpha$ radiation, intensities were estimated visually by comparison with a calibrated scale. Initially a total of 898 independent hkl reflexions were measured from the zero to the fourth layer about the b axis and brought to an approximate common scale by comparison with $0kl$ and $hk0$ reflexions about the a and c axes and with hhl reflexions measured from the zero-layer photograph about $[1\bar{1}0]$. After correction for the Lorentz–polarization effect these limited data were used to solve the structure but later a larger set of data was collected, including the layers for $k = 5$ and 6, with much extended exposures. This set, which contained 1727 reflexions, was corrected for the usual Lorentz–polarization effect and also for spot shape (Phillips, 1956). No correction for absorption was made to either set of data as μ is only ~ 5. The scale factor and an overall temperature factor were obtained from a Wilson plot.

Determination of the structure

The difficulties inherent in solving structures of molecules entirely composed of light atoms especially in non-centrosymmetric space groups and particularly when the stereochemistry is unknown presented a daunting prospect. However, certain features of the diffraction pattern proved helpful in establishing the position and orientation of a large part of the molecular skeleton, although as will be described later these dominant features proved to be a hindrance in the use of superposition methods.

The evidence provided by high resolution mass spectrometry which gave an accurate molecular weight of 412·406 and the presence of eight methyl groups per molecule as determined by nuclear magnetic resonance strongly indicated that the molecule must be pentacyclic with a formula of $C_{30}H_{52}$ and must therefore be a triterpane. The melting point of 260° C is high and is exceeded by only one other known triterpane, namely gammacerane (m.p. 300° C) (Hills, Whitehead, Anders, Cummins & Robinson, 1966). These facts led to the belief that triterpane E might be closely related to gammacerane and a large number of trial structures were investigated for molecules possessing five fused six-membered rings. When the spiro configuration in ring A, a feature not hitherto reported in naturally occurring triterpanes, was revealed, it came as a result of the steady elimination of possible atomic sites.

The $N(z)$ intensity statistics test (Howells, Phillips & Rogers, 1950) yielded a non-centric distribution for the three-dimensional and $0kl$ sets of data but gave a distribution lying between the centric and hypercentric cases for the $h0l$ set of data. The choice of space group $C2$ was therefore endorsed since the enantiomorphic space groups Cm and $C2/m$ could also be ruled out on packing considerations. The curve for the $h0l$ data suggested that the molecule was lying on an apparent false centre of symmetry with each half of the molecule having approximately the same arrangement, as indeed the final solution shows.

The Patterson map was calculated on sharpened and unsharpened data using a sharpening function based upon $1/f^2$ for carbon. This function approximated to a quadratic expression in $(\sin^2\theta)$ and since the original short data did not extend beyond $\sin^2\theta = 0{\cdot}5$ where the weight of the function was about 50, no undue ripple caused by series termination effect was observed.

Inspection of the Patterson map showed numerous peaks along a line nearly parallel to the c axis at $u \sim 0$ and $\frac{1}{2}$ indicating the line of the length of the molecule. Furthermore the distribution of the peaks showed that the section at $v = 6/20$ was almost identical with that at $v = 0$ and that the sections at $v = 3/20$ and $9/20$ were similarly related. Also the peaks in the section $v = 3/20$ could be made coincident with those in the section $v = 0$ by a small translation parallel to the c axis. A dominant peak in this latter section was readily identified as one of the C–C bonds of about 1·5 Å and together with another large peak of about equal weight on the v axis in the 6/20 section and other substantial peaks within 3 Å of the origin it was established that the molecule did indeed possess a skeleton of fused rings. From the weights and position of these peaks it was possible to deduce that the molecule possessed four such fused rings and that at least three were in the all-chair all-*trans* configuration with the mean plane of the rings practically parallel to the b axis. The resolution of the Patterson map was such that it was possible to say that there existed in the molecule nine C–C distances of the type C(6)–C(7), ten distances of the type C(6)–C(10) and five axial vectors of 1·54 Å. Numerous other vectors were identified, which while confirming the arrangement of four fused rings, did not disclose the orientation of the fifth ring.

At this point the computer application of superposition methods would have been welcome but no program was available until after the structure had been solved. Instead hand tracings of the Patterson map were employed to create the sum function (Buerger, 1959), which gave surprisingly good resolution over a large part of the molecule.

The dominant 200 and 0,0,14 reflexions, which are the first and third strongest reflexions, were useful in deciding the approximate position of the molecule in the unit cell. For instance, from inspection of peaks in the Patterson map and from packing considerations it was certain that the sign of the 200 reflexion must be negative thus placing the molecule nearly in the plane $\frac{1}{4}yz$. Similarly, in order to accommodate a fused ring skeleton on the (100) plane the sign of the 0,0,14 had to be positive. As an initial trial structure, the structure factor calculation was made for the $0kl$ data using 24 atoms, 22 of which were in a ring system of five fused all-chair all-*trans* six membered rings such as gammacerane plus a methyl group at each end. This yielded an R of 0·57 but the phased F_o map clearly showed the first four rings and indicated the fifth ring roughly at right angles to the other four. The best of several other trial structures on this projection gave an R of 0·43. This structure had three rings all-chair all-*trans*, later identified as E D and C, ring B boat and ring A chair but *cis* to B.

Before attempting three-dimensional calculations some two-dimensional projections on (010) were calculated using the six strongest $h0l$ reflexions, including the 200 and 0,0,14 whose signs had already been deduced. The signs of the remainder were systematically varied, taking into account the arbitrary signs of a chosen pair of reflexions to fix the origin. The best looking map gave groups of density corresponding to the ring junction positions, which could be clearly seen for four rings. By estimating the x coordinates and taking the z coordinates from the best (100) trial structure, a structure factor calculation for all the $h0l$ data yielded $R\sim 0·60$. From the structure factor list a selection was made of 47 reflexions, whose signs were considered to be probably correct. The Fourier synthesis based on these 47 reflexions is shown in Fig. 1 in which most of the molecule is clearly visible. Moreover, the map not only indicated that one methyl group was wrongly placed at X, but also showed likely positions for other side groups at Y both of which were soon proved to be correct. The small peak on the 2_1 axis at $x=\frac{1}{4}$, $z=\frac{1}{2}$ was dismissed as Fourier noise although in the end it was shown that there were two methyl groups close to this axis. The distorted peak of the A–B ring junction (though at this stage the ends of the molecule could not be distinguished) compared with the other ring junction peaks was the result of the *cis*-junction of the trial structure, whilst the endmost peak of ring A appeared to contain perhaps three atom sites. Speculative interpretation suggested the existence of an isopropyl group but the high melting point of the compound could be taken as contrary evidence. The remaining atoms of ring A were not revealed.

Henceforward enough was known about the position of a major part of the ring skeleton to justify three-dimensional calculations. Suitable Harker vectors in the $P(u0w)$ Patterson section were selected to satisfy the C(20) and C(22) positions indicated in the (010) F_o projection and model building enabled a large part of the molecule to be assembled. Many trial structures were refined by least-squares methods, during the course of which the side methyl groups C(27) and C(23) were definitely established and the methyl group C(26) confirmed. Furthermore the geminal methyl pair C(29) and C(30) and the lone methyl group C(28) were also confirmed as true sites, making the first ring E and therefore the ring with unknown configuration, A. This choice was felt initially to be doubtful as most reported triterpanes showed that modifications were more likely in ring E than ring A. However changing the positions of the geminal methyl pair and the C(28) methyl group to make the first ring A resulted in a marked rejection of the latter, *i.e.* very high temperature factor, but a much less marked rejection of the geminal pair. Additionally the overall R index for such trial structures was generally worse.

Trial structures were refined by three or four cycles of structure-factor least-squares procedures followed by F_o and difference maps. If a trial structure contained less than thirty atoms, the observed structure amplitudes were weighted by a method according to

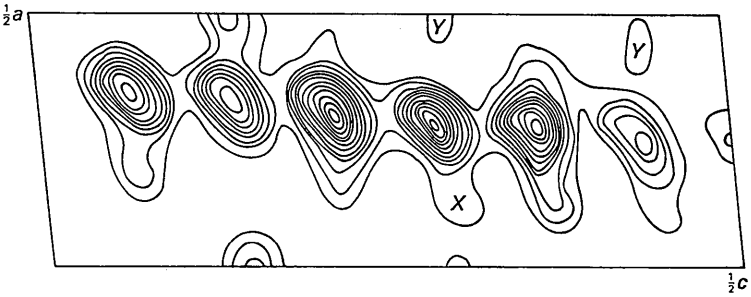


Fig. 1. F_o projection on (010) from the first trial structure using signs from 47 reflexions. Contours at arbitrary intervals.

Sim (1959) although the expected improvement in resolution did not materialize. The early trial structures were composed of *trans*-fused *C*, *D* and *E* rings, *B* ring boat and fixed side methyl groups C(23), C(26), C(27), C(28), C(29) and C(30). This arrangement permitted ring *A* to be fused at C(5) with its

Table 1. *Observed and calculated structure factors*

Each column contains the running index *l*, F_{obs}, F_{calc} and α (in degrees). F_{obs} and F_{calc} are full scale.

H= 0	K= 0		
1	13	4	0
2	111	88	180
3	8	8	180
4	84	62	180
5	9	8	180
6	57	46	180
7	50	54	180
8	51	41	180
9	55	56	180
10	64	54	180
11	43	29	180
12	110	89	180
13	60	57	180
14	231	162	0
15	30	18	0
16	7	4	180
17	1	4	180
18	4	3	0
19	12	12	0
20	4	4	0
21	6	5	180
H= 2	K= 0		
0	276	281	180
1	125	122	0
2	156	177	0
3	13	12	0
4	71	41	0
5	34	30	0
6	64	55	180
7	74	69	0
8	38	35	0
9	6	5	180
10	8	8	0
11	35	32	180
12	48	33	0
13	39	30	180
14	134	103	180
15	19	11	0
16	33	30	0
17	9	4	0
18	16	17	0
19	3	4	0
20	13	16	180
21	15	14	0
22	4	5	0
-1	104	106	180
-2	26	19	180
-3	49	39	180
-4	54	53	180
-5	11	9	180
-6	23	28	0
-7	87	68	0
-8	34	20	180
-9	6	7	180
-10	15	16	0
-11	17	17	0
-12	35	27	0
-13	73	51	0
-14	35	28	180
-15	14	9	180
-16	23	19	180
-17	1	2	180
-18	14	16	180
-19	4	10	180
-20	12	6	0
-21	20	17	0
-22	8	8	0
-23	2	2	180
-24	2	3	180
-25	17	20	0
-26	18	27	180
-27	5	12	180
H= 4	K= 0		
0	55	56	0
1	131	137	180
2	90	90	180
3	25	23	0
4	1	3	180
5	37	33	0
6	3	11	0
7	55	38	0
8	32	27	0
9	6	8	0
10	4	3	0
11	11	10	0
12	3	2	180
13	18	20	0
14	54	54	0
15	48	54	180
16	37	48	180
17	4	8	180
18	12	13	180
19	6	6	0
20	3	7	180
21	10	14	0
22	5	6	0
23	7	8	0
-1	52	54	0
-2	39	34	180
-3	8	10	0
-4	34	21	180
-5	46	33	180
-6	74	58	0
-7	12	19	180
-8	4	3	0
-9	10	9	180
-10	10	8	0
-11	6	8	0
-12	18	13	0
-13	19	13	0
-14	3	2	0
-15	25	22	0
-16	3	5	180
-17	16	15	0
-18	17	14	180
-19	18	15	180
-20	35	29	0
-21	14	13	180
-22	4	7	180
-23	21	26	180
-24	8	10	180
-25	27	26	180
-26	7	7	0
-27	22	25	0
H= 6	K= 0		
0	8	9	180
1	106	97	0
2	19	13	0
3	61	60	180
4	11	12	180
5	34	37	180
6	2	3	180
7	1	1	180
8	2	6	180
9	10	11	180
10	10	9	180
11	2	3	180
12	16	18	0
13	17	19	180
14	13	15	180
15	54	67	0
16	20	22	0
17	10	13	180
18	4	7	180
19	7	10	180
-1	9	12	180
-2	23	18	0
-3	3	3	0
-4	14	15	0
-5	16	10	180
-6	1	3	180
-7	17	13	0
-8	3	8	0
-9	1	2	180
-10	2	4	180
-11	10	10	180
-12	2	2	180
-13	4	5	0
-14	11	11	180
-15	4	7	180
-16	3	6	180
-17	9	10	180
-18	13	12	0
-19	9	11	180
-20	2	2	180
-21	2	2	180
-22	0	4	180
-23	11	13	0
-24	2	4	180
-25	26	23	0
-26	13	12	0
-27	6	6	180
H= 8	K= 0		
0	10	10	180
1	9	8	180
2	9	7	0
3	16	13	0
4	2	1	180
5	4	2	0
6	9	9	0
7	16	16	180
8	9	7	0
9	12	12	0
10	3	3	180
11	2	1	180
12	11	12	180
13	10	9	0
14	2	3	180
15	24	24	180
16	4	3	0
17	13	14	0
18	4	2	0
19	6	6	0
20	4	3	0
21	5	7	180
-1	4	2	0
-2	18	13	180
-3	3	4	180
-4	8	10	180
-5	14	15	0
-6	9	9	0
-7	2	1	180
-8	11	13	0
-9	4	4	0
-10	6	5	0
-11	15	20	180
-12	8	11	180
-13	16	18	0
-14	2	1	180
-15	2	6	180
-16	2	6	180
-17	3	4	180
-18	2	6	180
-19	4	4	0
-20	2	2	180
-21	8	8	0
-22	8	5	0
-23	10	10	0
-24	9	10	0
-25	12	14	180
-26	8	10	180
-27	5	6	0
H= 10	K= 0		
0	8	8	0
1	3	2	180
2	5	4	180
-1	5	2	0
-2	5	3	0
-3	6	6	180
-4	2	1	180
-5	7	5	0
-6	4	3	0
-7	4	5	180
-8	7	10	180
-9	6	8	180
-10	13	12	180
-11	10	9	0
-12	11	9	0
-13	5	4	180
-14	5	3	0
-15	4	4	0
-16	6	8	0
-17	4	6	180
-18	4	2	0
-19	10	4	0
-20	8	7	0
-21	3	2	0
-22	2	5	180
-23	6	7	180
-24	9	11	180
-25	1	3	180
-26	7	6	0
H= 1	K= 1		
0	39	44	298
1	243	287	267
2	57	59	47
3	47	39	387
4	112	86	18
5	46	42	36
6	40	32	7
7	73	65	230
8	15	17	112
9	30	27	39
10	17	19	124
11	15	18	196
12	2	6	181
13	77	66	104
14	46	36	197
15	63	52	253
16	2	6	180
17	13	10	291
18	17	14	12
19	17	20	28
20	15	15	25
21	13	17	207
22	2	2	336
23	6	6	36
24	13	10	36
25	9	10	244
26	5	6	122
-1	146	145	88
-2	13	14	200
-3	66	62	92
-4	72	63	194
-5	85	74	102
-6	42	68	141
-7	78	57	250
-8	14	13	110
-9	33	21	190
-10	43	34	44
-11	7	6	319
-12	17	13	57
-13	75	61	272
-14	41	31	313
-15	35	31	39
-16	13	17	3
-17	26	19	49
-18	7	9	242
-19	28	28	162
-20	19	19	200
-21	18	20	251
-22	9	9	115
-23	5	6	238
-24	9	10	114
-25	3	1	155
-26	11	13	303
-27	13	17	51
-28	7	10	191
-29	4	2	170
-30	5	6	26
H= 3	K= 1		
0	58	78	138
1	44	63	93
2	44	40	344
3	24	20	338
4	6	9	231
5	13	17	313
6	22	18	262
7	3	13	44
8	18	22	241
9	8	1	189
10	7	9	305
11	6	7	245
12	2	1	187
13	15	16	310
14	14	16	121
15	28	35	113
16	6	5	253
17	10	9	51
18	8	10	223
19	7	7	259
20	7	8	287
21	11	12	7
22	4	4	18
23	3	2	230
-1	33	23	39
-2	20	18	239
-3	25	23	66
-4	49	45	253
-5	26	21	336
-6	12	17	285
-7	38	27	185
-8	30	22	232
-9	9	7	227
-10	6	5	321
-11	5	2	18
-12	28	24	42
-13	20	18	246
-14	20	17	175
-15	23	24	65
-16	10	7	179
-17	15	16	67
-18	21	17	258
-19	14	13	356
-20	9	10	12
-21	3	4	118
-22	5	7	296
-23	4	3	61
-24	6	8	310
-25	9	13	45
-26	23	21	112
-27	29	30	214
-28	10	10	255
H= 5	K= 1		
0	61	56	274
1	61	55	215
2	73	74	110
3	9	11	120
4	17	23	78
5	17	15	216
6	7	9	45
7	12	16	58
8	13	17	241
9	17	16	32
10	4	5	339
11	14	17	1
12	5	6	342
13	7	9	81
14	29	37	287
15	24	27	264
16	23	27	93
17	5	7	122
18	11	12	81
19	10	12	215
20	6	7	129
21	5	6	165
22	8	10	220
23	5	6	67
24	4	2	270
25	6	5	46
-1	7	8	172
-2	9	8	276
-3	11	13	307
-4	23	24	43
-5	14	14	251
-6	13	15	231
-7	10	12	324
-8	20	27	52
-9	10	11	348
-10	9	10	13
-11	13	14	32
-12	5	10	99
-13	4	5	109
-14	9	10	225
-15	8	8	174
-16	6	6	23
-17	8	6	213
-18	17	20	88
-19	15	17	214
-20	7	7	168
-21	15	15	245
-22	12	11	83
-23	4	1	283
-24	4	7	192
-25	11	11	161
-26	20	19	275
-27	20	19	359
-28	5	5	30
-29	3	2	293
-30	8	7	25
H= 7	K= 1		
0	10	10	102
1	14	17	336
2	26	32	285
3	5	5	211
4	6	5	55
5	6	5	343
6	11	11	84
7	3	3	91
8	16	15	244
9	8	8	134
10	7	7	73
11	16	10	95
12	4	2	148
13	10	10	245
14	22	23	163
15	4	2	298
16	18	21	284
17	4	3	289
18	3	3	284
19	4	5	15
20	5	6	76
21	3	3	23
22	6	6	255
23	5	3	199
-1	9	8	251
-2	3	3	139
-3	6	6	70
-4	13	12	84
-5	8	8	183
-6	20	18	229
-7	4	16	95
-8	3	2	113
-9	3	4	61
-10	2	4	7
-11	8	9	355
-12	7	9	88
-13	6	3	158
-14	7	10	286
-15	3	4	347
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-9	9	8	284
-10	3	4	307
-11	3	2	213
-12	13	13	292
-13	11	10	66
-14	12	14	22
-15	19	21	311
-16	14	14	240
-17	7	9	159
-18	8	9	189
-19	3	4	286
-20	9	8	109
-21	8	9	59
-22	10	10	41
-23	10	10	225
-24	5	4	86
-25	4	5	212
-26	4	2	279
H= 3	K= 5		
0	11	12	190
1	13	13	254
2	8	10	92
3	4	5	351
4	4	3	72
5	7	9	171
6	9	9	264
7	5	6	328
8	5	6	117
9	7	8	312
10	6	9	164
11	6	7	249
12	7	9	15
13	7	8	78
14	4	4	210
15	6	6	270
16	6	7	167
17	7	7	55
18	7	8	51
19	3	4	142
20	3	4	325
21	6	7	312
22	4	3	345
23	6	6	245
-1	18	15	147
-2	23	23	53
-3	11	11	305
-4	3	4	133
-5	18	19	349
-6	12	12	6
-7	9	7	312
-8	16	15	217
-9	11	12	95
-10	11	11	230
-11	7	7	294
-12	5	7	57
-13	8	9	233
-14	7	8	140
-15	8	9	180
-16	6	8	104
-17	3	1	23
-18	8	5	118
-19	6	7	15
-20	10	10	356
-21	7	7	290
-22	8	8	213
-23	4	4	64
-24	6	5	252
-25	5	5	355
-26	4	1	305
-27	7	7	184
-28	10	9	97
-29	7	7	6
-30	6	4	259
H= 5	K= 5		
0	9	10	89
1	14	16	109
2	10	11	275
3	11	13	191
4	10	12	128
5	8	9	133
6	5	6	78
7	3	4	40
8	5	5	38
9	4	4	251
10	4	5	309
11	5	4	229
12	6	6	245
13	11	12	334
14	3	3	47
15	10	9	75
16	14	12	301
17	11	11	233
18	8	7	159
19	6	5	134
20	7	5	99
-1	17	22	9
-2	13	15	269
-3	3	3	194
-4	10	11	286
-5	11	12	260
-6	5	2	114
-7	7	6	55
-8	11	10	341
-9	5	4	214
-10	6	5	125
-11	5	6	189
-12	5	4	310
-13	7	8	108
-14	6	7	138
-15	6	6	73
-16	3	2	279
-17	5	4	101
-18	8	8	255
-19	6	4	221
-20	3	2	158
-21	4	5	82
-22	8	8	350
-23	3	1	127
-24	3	3	127
-25	3	3	230
-26	5	3	7
-27	10	10	20
-28	8	7	290
-29	8	7	199
-30	4	2	144
H= 7	K= 5		
0	11	13	294
1	14	15	0
2	11	12	29
3	8	9	321
4	7	8	239
5	3	3	201
6	5	4	349
7	3	2	189
8	7	7	149
9	6	7	68
10	5	5	250
11	5	4	260
12	10	10	105
13	14	12	168
14	6	7	264
15	4	3	302
16	9	8	64
17	7	7	15
18	7	6	263
19	3	3	231
20	4	4	327
21	2	2	271
22	4	5	119
-1	12	12	193
-2	11	12	113
-3	8	10	252
-4	6	4	320
-5	10	10	93
-6	8	7	142
-7	3	3	112
-8	5	4	178
-9	6	6	143
-10	6	8	167
-11	7	7	248
-12	6	6	26
-13	5	6	345
-14	3	3	308
-15	6	5	25
-16	3	3	190
-17	7	5	255
-18	8	7	344
-19	3	4	13
-20	4	5	69
-21	2	1	274
-22	2	2	165
-23	2	2	242
-24	2	4	170
-25	2	2	272
-26	2	3	4
-27	7	7	223
-28	6	6	154
-29	4	5	55
H= 9	K= 5		
0	5	4	104
1	6	7	197
2	4	3	195
3	3	4	16
4	6	5	303
5	3	3	289
6	3	4	90
7	2	2	219
8	2	1	278
9	2	2	300
10	2	3	24
11	2	4	125
12	2	4	236
13	2	6	13
14	4	4	81
15	6	4	195
16	4	3	267
17	3	2	169
18	3	2	24
-1	4	3	11
-2	4	2	239
-3	4	5	124
-4	4	1	267
-5	4	5	325
-6	4	3	298
-7	4	4	183
-8	3	6	85
-9	4	3	208
-10	4	5	271
-11	4	4	332
-12	6	4	131
-13	7	6	66
-14	6	5	338
-15	4	4	231
H= 11	K= 5		
0	2	3	43
-1	6	2	125
-2	6	5	185
-3	4	5	240
-4	5	3	300
H= 0	K= 6		
0	34	47	358
1	29	38	284
2	35	42	215
3	37	41	128
4	16	19	7
5	9	9	92
6	11	13	87
7	7	9	303
8	7	7	93
9	5	4	76
10	12	15	29
11	16	21	111
12	12	14	181
13	7	8	261
14	18	21	10
15	19	22	302
16	14	18	219
17	12	15	151
18	7	9	332
19	6	7	84
20	3	4	72
21	3	4	200
22	3	4	229
23	3	2	156
24	3	1	82
25	7	8	263
26	3	3	42
27	3	3	24
H= 2	K= 6		
0	33	36	198
1	11	10	57
2	23	20	345
3	27	35	277.
4	16	17	183
5	7	9	167
6	14	15	229
7	5	5	111
8	7	8	300
9	3	5	27
10	7	6	161
11	16	18	321
12	18	22	33
13	17	19	115
14	15	15	196
15	11	12	101
16	15	15	7
17	16	19	308
18	7	7	167
19	5	6	235
20	7	8	232
-1	38	40	133
-2	39	39	62
-3	26	28	336
-4	13	13	118
-5	4	6	2
-6	11	11	304
-7	11	11	335
-8	6	5	258
-9	3	3	49
-10	4	3	76
-11	3	4	279
-12	7	8	286
-13	6	7	286
-14	13	16	213
-15	13	13	145
-16	9	10	103
-17	8	8	354
-18	8	10	123
-19	6	4	175
-20	3	3	223
-21	7	7	301
-22	3	2	303
-23	8	8	302
-24	8	7	1
-25	11	12	59
-26	6	4	153
-27	7	6	201
-28	2	2	78
-29	5	6	2
-30	4	3	231
H= 4	K= 6		
0	23	24	59
1	17	16	190
2	26	25	139
3	21	25	66
4	15	14	344
5	11	12	275
6	3	5	285
7	7	7	260
8	6	7	177
9	8	9	242
10	3	4	239
11	9	9	150
12	16	16	256
13	13	14	329
14	13	14	34
15	9	10	213
16	18	18	153
17	18	19	85
18	8	10	17
19	4	4	331
20	3	1	301
21	3	4	293
-1	23	24	337
-2	21	20	285
-3	16	15	148
-4	9	8	260
-5	7	7	262
-6	3	3	120
-7	3	4	119
-8	3	3	241
-9	6	7	180
-10	3	4	260
-11	5	2	252
-12	3	5	159
-13	6	5	279
-14	3	3	87
-15	4	4	346
-16	7	7	349
-17	7	6	184
-18	5	7	261
-19	4	3	241
-20	6	7	350
-21	6	6	32
-22	3	3	43
-23	9	10	107
-24	9	9	113
-25	8	8	190
-26	2	3	257
-27	7	8	360
-28	6	6	278
-29	4	6	199
H= 6	K= 6		
0	19	20	283
1	16	16	9
2	11	9	307
3	13	13	179
4	14	16	111
5	7	8	53
6	3	4	24
7	5	5	98
8	5	5	323
9	7	8	166
10	7	7	142
11	9	9	1
12	11	12	90
13	12	13	262
14	13	13	257
15	12	13	1
16	14	13	317
17	11	11	217
18	11	9	138
19	5	5	40
20	2	2	53
21	4	4	74
-1	14	16	215
-2	7	6	104
-3	13	14	351
-4	7	7	105
-5	6	5	183.
-6	3	3	239
-7	5	5	167
-8	3	3	328
-9	5	6	272
-10	3	2	71
-11	3	5	101
-12	3	4	117
-13	3	2	138
-14	6	2	241
-15	3	3	142
-16	6	3	293
-17	7	5	17
-18	4	6	58
-19	3	3	338
-20	3	2	165
-21	4	5	146
-22	5	3	98
-23	7	5	253
-24	8	8	271
-25	3	6	333
-26	4	2	20
H= 8	K= 6		
0	8	8	132
1	6	6	215
2	5	4	289
3	5	4	279
4	5	4	263
5	3	4	36
6	4	4	83
7	3	2	206
8	4	2	8
9	6	7	334
10	3	2	339
11	7	8	142
12	5	5	300
13	8	8	20
14	8	8	114
15	7	7	194
16	3	2	147
17	5	4	345
18	5	6	296
-1	6	5	10
-2	3	2	32
-3	6	8	136
-4	5	4	180
-5	3	3	254
-6	6	6	278
-7	5	5	264
-8	4	4	318
-9	8	10	22
-10	8	9	90
-11	7	6	178
-12	4	5	221
-13	5	5	44
-14	3	5	347
-15	3	4	287
-16	2	4	72
-17	2	4	83
-18	4	4	149
-19	3	4	194
-20	2	4	222
-21	4	5	254
-22	5	7	276
-23	5	7	341

plane perpendicular to the rest of the ring skeleton. Atom sites C(1) and C(4) were also kept fixed. It was found that C(5) could be moved substantially in the *x* direction with little change in the *R* index or in its own temperature factor. If a fused *A* ring were present then the C(1)–C(5) distance had to be greater than 2·4 Å and at least two atom sites had to be found in order to link C(1) with C(10) or C(6) and to account for the unresolved electron density observed in that region. The site of C(3) proved to be extremely vague, sometimes indicating two sites at different *y* values, sometimes one. Whilst the evidence for C(2) was non-existent, that for the C(24) methyl group, which appeared in only a few maps, occurred as a very small peak in the $z=\frac{1}{2}$ plane close to the 2_1 screw axis and was attributed to background ripple.

Most trial structures could be refined to an *R* of about 0·35 and as a result it became evident that C(1) was attached to C(5) by a single bond, thus making ring *B* strictly chair; also there was only one carbon atom attached to C(10), namely C(25). There still remained two atoms to be sited, by which time the evidence for C(2) was becoming stronger. With its inclusion in the calculations a further small improvement in *R* was obtained but the molecule now possessed an open end composed of C(1), C(2), C(3), C(4), C(5), C(10), C(23) and C(25) with the C(2)–C(3) distance greater than 2·3 Å. The position of C(25) was also problematic as it was neither part of a ring, nor of a methyl group at a ring junction. Further critical inspection of all the Fourier syntheses disclosed that the peak corresponding to C(24) was not exactly on the $z=\frac{1}{2}$ plane but had a coordinate of 0·494. When this atom was included in the calculations the *R* value fell immediately below 0·30. The C(2)–C(3) distance was still large but subsequent refinement showed that the *y* coordinates of C(3) and C(23) were too high. Following the adjustments of these coordinates the spiro configuration of ring *A* revealed itself and the isotropic refinement was continued until convergence was reached at $R=0{\cdot}20$. With the introduction of anisotropy for the carbon atoms there was no improvement in *R* and many of the anisotropic temperature factors became meaningless.

The extended data of 1727 reflexions were then introduced but again isotropic refinement of the carbon atoms alone would not reduce *R* below 0·21. However, for these data, meaningful anisotropic temperature factors enabled *R* to be reduced to a final value of 0·149 although convergence was very slow. The observed and calculated structure factors are listed in Table 1.

Refinement

The refinement of the structure was made using the block-diagonal approximation for carbon atoms alone with a 3×3 matrix for the positional parameters and a 1×1 or 6×6 matrix for the temperature factors. The overall scale factor was also refined with allowance for the interaction between it and the overall temperature factor. The weighting scheme was essentially unity for the trial structures but was changed to $w=1\Big/\left[1+\left(\frac{F_o-b}{a}\right)^2\right]$ where $a=4$ and $b=10$ when the correct structure had been obtained. The atomic scattering factors used were those published in *International Tables for X-ray Crystallography* (1962). Layer scaling was carried out at intervals by a method due to Eichorn (1956).

At the end of the refinement all x and z positional shifts were less than one tenth and the y coordinate shifts less than one quarter of their standard deviations, with a tendency towards randomness. The standard deviations of the anisotropic temperature factors were not available as an output of the least-squares program but all shifts were small again tending towards randomness, the largest shifts being in β_{22}.

In the absence of a large enough program the 52 hydrogen atoms could not be included in the calculations, but since they represent about 60% of the structure and contribute about 25% of the scattering power of the molecule, their exclusion from the refinement must account in part for the relatively high final R value. Their omission could explain some of the large discrepancies which exist between F_o and F_c, *e.g.* the 0,0,14 reflexion. A very high proportion of the carbon atoms are very close to this plane so that the 28 hydrogen atoms associated with the ring skeleton atoms would be scattering approximately in phase. In addition, this reflexion also suffers from the Renninger double diffraction effect from the 2,0,21 and $\bar{2}0\bar{7}$ reflexions although this contribution must be small.

Final difference and F_o Fourier syntheses were calculated which revealed the sites of about 20 hydrogen atoms principally those belonging to the carbon atoms of rings *B–E*.

During the isotropic refinement it was found necessary to hold the coordinates of C(2) constant in order to prevent the C(1)–C(2) distance from increasing and the C(2)–C(3) distance from decreasing abnormally. The introduction of anisotropy stopped this distortion but resulted in C(18) being displaced from an ideal position. The final list of positional parameters is given in Table 2 and the vibrational parameters in Table 3, which includes the isotropic B value from the last isotropic refinement cycle.

Table 2. *Fractional coordinates*

Standard deviations in brackets refer to last decimal place.

	x	y	z
C(1)	0·0989 (7)	0·2306 (13)	0·3691 (3)
C(2)	0·0687 (11)	0·1674 (22)	0·4148 (3)
C(3)	0·1926 (14)	0·1281 (14)	0·4445 (3)
C(4)	0·2807 (8)	0·2270 (12)	0·4216 (2)
C(5)	0·2401 (6)	0·2174 (10)	0·3710 (2)
C(6)	0·2731 (11)	0·0442 (12)	0·3485 (3)
C(7)	0·2410 (10)	0·0363 (11)	0·2992 (3)
C(8)	0·3018 (6)	0·1780 (9)	0·2742 (2)
C(9)	0·2644 (6)	0·3537 (9)	0·2936 (2)
C(10)	0·2927 (6)	0·3712 (10)	0·3441 (2)
C(11)	0·3132 (7)	0·5070 (9)	0·2683 (3)
C(12)	0·2815 (7)	0·5009 (9)	0·2179 (2)
C(13)	0·3163 (5)	0·3224 (9)	0·1982 (2)
C(14)	0·2559 (6)	0·1694 (9)	0·2227 (2)
C(15)	0·2934 (9)	−0·0022 (10)	0·2031 (2)
C(16)	0·2737 (10)	−0·0044 (10)	0·1514 (3)
C(17)	0·3419 (6)	0·1358 (10)	0·1299 (2)
C(18)	0·2963 (6)	0·3197 (9)	0·1462 (2)
C(19)	0·3448 (7)	0·4664 (10)	0·1232 (2)
C(20)	0·3241 (6)	0·4592 (10)	0·0714 (2)
C(21)	0·3633 (6)	0·2801 (11)	0·0542 (2)
C(22)	0·3141 (8)	0·1302 (11)	0·0791 (2)
C(23)	0·4133 (9)	0·1725 (23)	0·4372 (3)
C(24)	0·1909 (13)	0·1591 (16)	0·4938 (4)
C(25)	0·2563 (8)	0·5483 (12)	0·3613 (3)
C(26)	0·4414 (7)	0·1623 (13)	0·2839 (2)
C(27)	0·1172 (6)	0·1831 (11)	0·2127 (2)
C(28)	0·4831 (8)	0·1210 (13)	0·1428 (3)
C(29)	0·1899 (7)	0·4855 (12)	0·0546 (3)
C(30)	0·3988 (9)	0·5980 (12)	0·0518 (3)

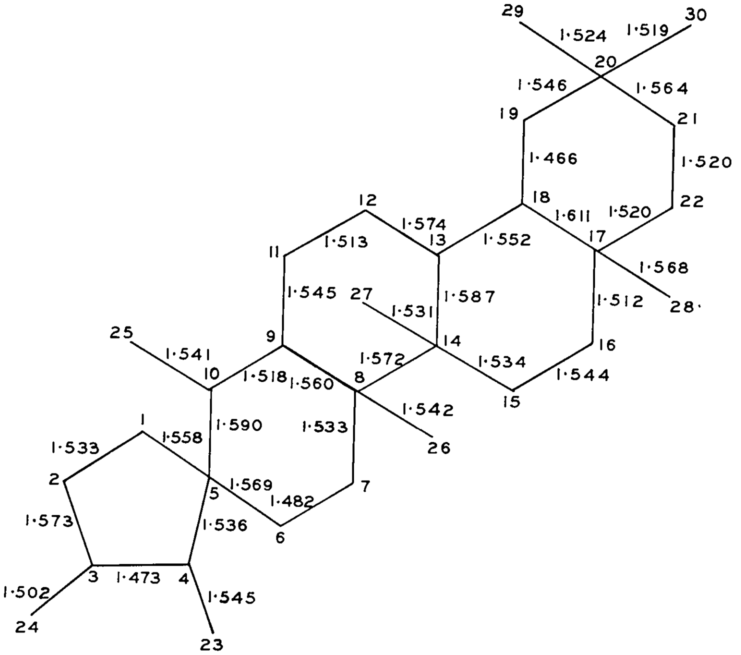


Fig. 2. Interatomic distances.

Discussion of the results

Fourier and difference maps were used extensively for the trial structures but in the absence of stereochemical knowledge of the molecule the location of some of the carbon atoms from these maps was difficult. In all the maps there appeared peaks in the background of approximately 0·6 e.Å^{-3}, arising it would seem from the large contribution of the (0,0,14) plane. Often such positions could have been interpreted as carbon atom sites, especially those near the ring junction atoms, but other positions such as those near the peripheral atoms of the ring skeleton, *e.g.* C(6), C(7), C(11), C(12), C(15), C(16), could only be associated with hydrogen atom sites. In retrospect – and our experience has been supported by the determination of the structures of two

Table 3. *Thermal parameters*

Anisotropic temperature factors are given by $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hl\beta_{13}+kl\beta_{23}+hk\beta_{12})\right]$.

B is the isotropic temperature factor at the end of the last isotropic refinement cycle

	B	β_{11}	β_{22}	β_{33}	β_{13}	β_{23}	β_{12}
C(1)	5·41 Å^2	0·0135	0·0262	0·0018	0·0021	−0·0006	−0·0041
C(2)	8·43	0·0242	0·0633	0·0019	0·0070	0·0087	0·0015
C(3)	6·65	0·0224	0·0291	0·0015	0·0032	0·0016	0·0041
C(4)	5·57	0·0177	0·0306	0·0010	0·0013	0·0001	0·0030
C(5)	4·41	0·0141	0·0188	0·0011	−0·0003	0·0012	0·0023
C(6)	6·43	0·0306	0·0167	0·0013	0·0020	0·0016	0·0036
C(7)	6·44	0·0278	0·0129	0·0017	0·0026	0·0015	−0·0057
C(8)	4·05	0·0121	0·0177	0·0011	0·0009	−0·0015	0·0055
C(9)	3·78	0·0110	0·0167	0·0011	0·0011	0·0002	−0·0055
C(10)	3·82	0·0120	0·0173	0·0011	0·0002	0·0003	0·0003
C(11)	4·83	0·0139	0·0141	0·0017	0·0009	−0·0004	−0·0094
C(12)	4·05	0·0180	0·0133	0·0009	0·0015	−0·0017	0·0009
C(13)	3·15	0·0080	0·0141	0·0013	0·0012	−0·0017	0·0046
C(14)	4·16	0·0118	0·0148	0·0012	0·0009	0·0001	0·0029
C(15)	5·81	0·0275	0·0129	0·0010	0·0038	−0·0009	0·0108
C(16)	6·58	0·0290	0·0097	0·0017	0·0046	−0·0004	−0·0004
C(17)	3·98	0·0149	0·0135	0·0011	0·0016	−0·0013	0·0152
C(18)	4·12	0·0098	0·0164	0·0014	0·0013	−0·0014	0·0043
C(19)	4·44	0·0153	0·0142	0·0015	0·0023	−0·0012	−0·0010
C(20)	3·95	0·0142	0·0209	0·0008	0·0023	−0·0011	−0·0002
C(21)	4·13	0·0142	0·0194	0·0015	0·0025	−0·0009	0·0051
C(22)	5·64	0·0228	0·0188	0·0013	0·0008	−0·0012	−0·0016
C(23)	8·59	0·0177	0·0748	0·0018	−0·0021	0·0041	0·0139
C(24)	9·01	0·0378	0·0271	0·0024	0·0089	0·0050	−0·0002
C(25)	5·05	0·0203	0·0179	0·0016	0·0034	−0·0042	0·0005
C(26)	5·05	0·0175	0·0382	0·0011	0·0005	0·0011	0·0336
C(27)	4·01	0·0123	0·0239	0·0012	0·0019	−0·0013	−0·0136
C(28)	6·43	0·0178	0·0311	0·0018	0·0040	0·0005	0·0260
C(29)	4·99	0·0147	0·0277	0·0016	0·0032	0·0030	0·0112
C(30)	6·44	0·0209	0·0220	0·0021	0·0059	−0·0008	−0·0120

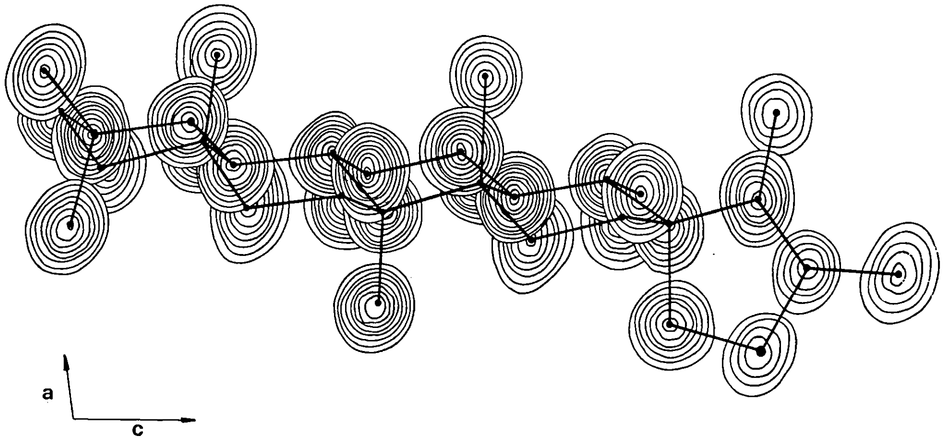


Fig. 3. Superimposed sections of the electron density parallel to (010). The sections have been displaced along the +*a* axis corresponding to a 10° tilt away from the *b* axis to disperse atom centres. Contours start at 1 e.Å^{-3} and are drawn at intervals of 0·5 e.Å^{-3}.

more triterpanes – the use of a shortened data list can reveal hydrogen atom sites even with $R \sim 0·35$. By contrast there was great difficulty in finding C(2) and C(24). Their residual peak heights never exceeded 0·6 e.Å^{-3} and in most cases were lost entirely in the background. It is noteworthy that these two atoms have high isotropic temperature factors.

After the refinement of each trial structure, atoms were accepted or rejected on the basis of temperature factor and molecular geometry. These criteria were not always strong enough to distinguish between true and false sites. Thus the decision on whether the unmodified end ring was *A* or *E* was made upon the rejection of C(28) when bonded to C(18) and much less so on the positions of the geminal methyl pair when attached to C(22) where both C(29) and C(30) were acceptable. The indeterminacy of the true coordinates of C(3) and C(5) was also difficult to overcome.

Fortunately the orientation of the molecule was clearly revealed in the Patterson function but the very regular and repetitive nature of the rings hindered, if not prevented, a complete successful determination by superposition methods. Hand tracings of the Patterson function were used in the early stages to produce a modified form of the sum function and although the discriminatory powers of this type of function are known to be poor, nevertheless the maps did show a surprising amount of the molecule. As a start, Harker peaks were identified in the section $P(u0w)$ corresponding to the symmetry vectors of C(17) and C(22) [or C(19), and C(20)] from which non-Harker peaks were found for many of the other ring atoms C(5)–C(21). Using the C(22) Harker peak as origin peak, tracings of the sections $v=0$, 3/20, 6/20 and 9/20 of the Patterson function were superimposed and points plotted where overlap of peaks occurred. A concentration of points indicated a probable atomic centre, and if this position could be associated with a Harker peak and was stereochemically sound, then the process was continued with the new point as a superposition origin. In this way, the positions of all the ring atoms C(5)–C(22) were found as well as the methyl groups C(26)–C(30). However the vectors associated with the spiro ring *A* were masked and in this region the only discernible feature, comparatively ill determined, was a fifth ring in the same chair configuration as the other four. Many additional peaks similar to those in the F_o maps were also present especially associated with the ring junction atoms.

After the correct structure had been obtained, a computer program of the minimum function became available (Nordman, 1967) and two attempts at multiple superposition were made. In the first the positions of thirteen carbon atoms comprising the *D* and *E* rings and C(8), C(26) and C(27) were input and a 26-fold superposition calculated. The second attempt contained the rings, *B*, *C*, *D* and *E* plus C(1), C(4), C(26) and C(27) and a 44-fold superposition performed. The resulting minimum functions were in each case little better than the hand traces of the sum function. Again the spiro ring was not revealed but ring *A* appeared as a fused chair ring and the usual spurious peaks were present. It would appear that for molecules made up of repetitive units in a regular fashion the likelihood of total success with the superposition method is not high.

The bond distances and bond angles with their standard deviations are listed in Tables 4 and 5 and Fig. 2. The average bond distance of 34 C–C bonds is 1·540 Å with an overall standard deviation of 0·031 Å, compared with the mean of the standard deviations of the individual bond lengths of 0·011 Å. The mean value of 59 tetrahedral angles is 110·92° with an overall standard deviation of 3·29°. The mean of the standard deviations of the individual angles is 0·39°. Thus although the block-diagonal approximation gives lower standard deviations for individual bonds and angles, at the 3σ level for the overall standard deviations no bond distance or bond angle is significantly different from the mean value or indeed from the ideal values. As a result the molecular skeleton comprising rings *B*, *C*, *D* and *E* is very regular (Figs. 3 and 4). The greatest deviation occurs at C(18) which, as mentioned earlier, became displaced with the introduction of anisotropic temperature factors.

Table 4. *Interatomic distances*

Standard deviations in brackets refer to the last decimal positions.

C(1)—C(2)	1·533 (12) Å
C(1)—C(5)	1·558 (10)
C(2)—C(3)	1·573 (16)
C(3)—C(4)	1·473 (13)
C(3)—C(24)	1·502 (14)
C(4)—C(5)	1·536 (9)
C(4)—C(23)	1·545 (13)
C(5)—C(6)	1·569 (12)
C(5)—C(10)	1·590 (10)
C(6)—C(7)	1·482 (12)
C(7)—C(8)	1·533 (11)
C(8)—C(9)	1·560 (10)
C(8)—C(14)	1·572 (8)
C(8)—C(26)	1·542 (10)
C(9)—C(10)	1·518 (9)
C(9)—C(11)	1·545 (10)
C(10)–C(25)	1·541 (11)
C(11)–C(12)	1·513 (10)
C(12)–C(13)	1·574 (9)
C(13)–C(14)	1·587 (10)
C(13)–C(18)	1·552 (9)
C(14)–C(15)	1·534 (10)
C(14)–C(27)	1·531 (9)
C(15)–C(16)	1·544 (11)
C(16)–C(17)	1·512 (12)
C(17)–C(18)	1·611 (9)
C(17)–C(22)	1·520 (10)
C(17)–C(28)	1·568 (11)
C(18)–C(19)	1·466 (11)
C(19)–C(20)	1·546 (9)
C(20)–C(21)	1·564 (11)
C(20)–C(29)	1·524 (11)
C(20)–C(30)	1·519 (11)
C(21)–C(22)	1·520 (12)

Table 5. *Bond angles*

Standard deviations are given in brackets.

C(2)—C(1)—C(5)	105·6 (0·4)
C(1)—C(2)—C(3)	107·6 (0·5)
C(2)—C(3)—C(4)	102·4 (0·4)
C(2)—C(3)—C(24)	114·6 (0·7)
C(4)—C(3)—C(24)	117·4 (0·6)
C(3)—C(4)—C(5)	107·6 (0·5)
C(3)—C(4)—C(23)	111·8 (0·5)
C(5)—C(4)—C(23)	116·3 (0·4)
C(1)—C(5)—C(4)	102·1 (0·4)
C(1)—C(5)—C(6)	108·9 (0·5)
C(1)—C(5)—C(10)	110·9 (0·4)
C(4)—C(5)—C(6)	114·4 (0·4)
C(4)—C(5)—C(10)	112·5 (0·4)
C(6)—C(5)—C(10)	108·0 (0·3)
C(5)—C(6)—C(7)	115·2 (0·2)
C(6)—C(7)—C(8)	113·1 (0·5)
C(7)—C(8)—C(9)	107·2 (0·3)
C(7)—C(8)—C(14)	110·0 (0·4)
C(7)—C(8)—C(26)	109·7 (0·4)
C(9)—C(8)—C(14)	109·7 (0·4)
C(9)—C(8)—C(26)	107·6 (0·4)
C(14)-C(8)—C(26)	112·5 (0·3)
C(8)—C(9)—C(10)	114·8 (0·4)
C(8)—C(9)—C(11)	111·6 (0·3)

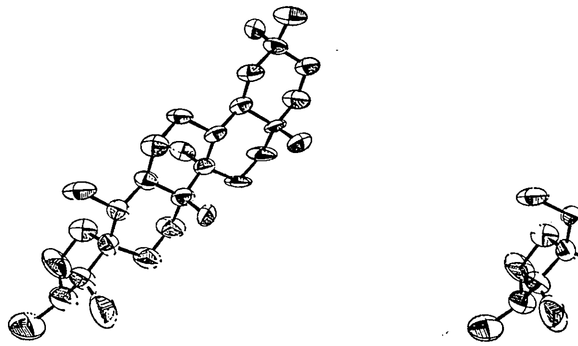
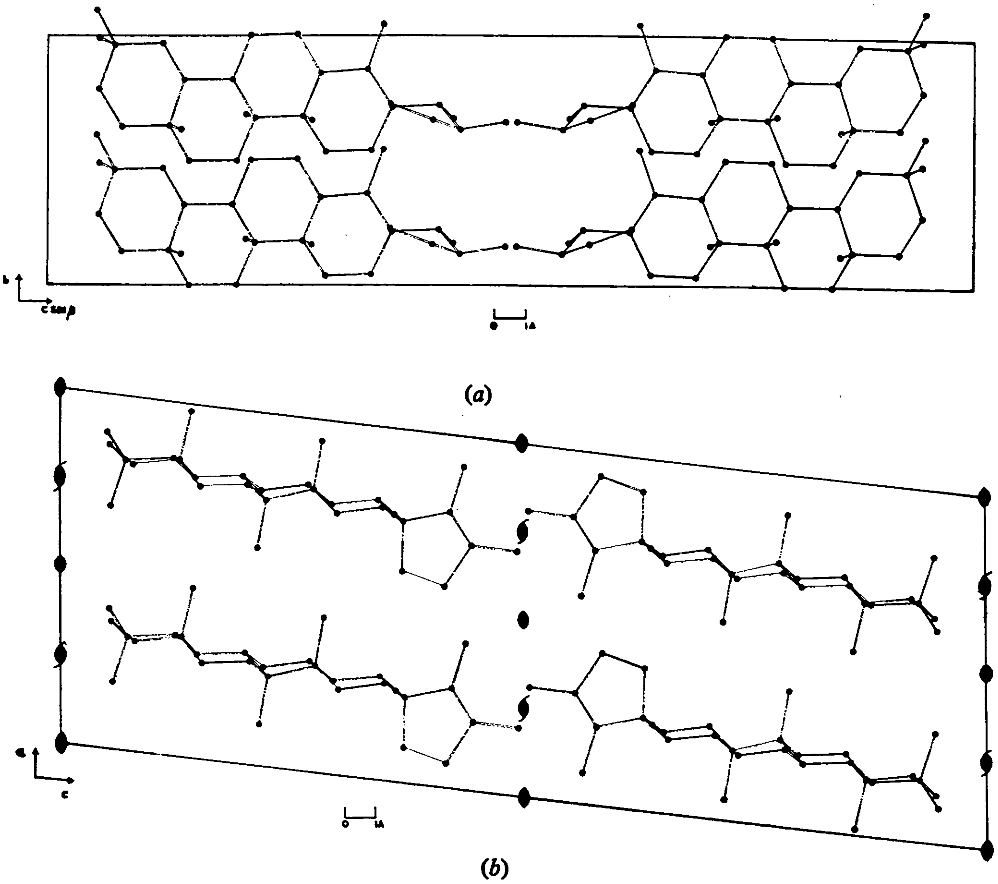


Fig. 4. Stereoscopic view of triterpane *E* (Johnson, 1965).



(*a*)

(*b*)

Fig. 5. Projection of one unit cell (*a*) on to the (100) plane (*b*) on to the (010) plane.

Table 5 (*cont.*)

C(10)–C(9)—C(11)	112·3 (0·4)
C(5)—C(10)–C(9)	113·2 (0·4)
C(5)—C(10)–C(25)	112·1 (0·3)
C(9)—C(10)–C(25)	112·6 (0·4)
C(9)—C(11)–C(12)	114·5 (0·4)
C(11)–C(12)–C(13)	111·4 (0·4)
C(12)–C(13)–C(14)	110·6 (0·3)
C(12)–C(13)–C(18)	112·2 (0·3)
C(14)–C(13)–C(18)	116·0 (0·4)
C(8)—C(14)–C(13)	108·6 (0·3)
C(8)—C(14)–C(15)	110·1 (0·3)
C(8)—C(14)–C(27)	113·0 (0·3)
C(13)–C(14)–C(15)	109·1 (0·3)
C(13)–C(14)–C(27)	108·9 (0·3)
C(15)–C(14)–C(27)	107·2 (0·4)
C(14)–C(15)–C(16)	112·5 (0·4)
C(15)–C(16)–C(17)	113·7 (0·5)
C(16)–C(17)–C(18)	108·7 (0·3)
C(16)–C(17)–C(22)	110·8 (0·5)
C(16)–C(17)–C(28)	111·9 (0·4)
C(18)–C(17)–C(22)	107·2 (0·4)
C(18)–C(17)–C(28)	109·1 (0·4)
C(22)–C(17)–C(28)	109·0 (0·3)
C(13)–C(18)–C(17)	107·7 (0·3)
C(13)–C(18)–C(19)	116·5 (0·4)
C(17)–C(18)–C(19)	113·8 (0·3)
C(18)–C(19)–C(20)	115·1 (0·4)
C(19)–C(20)–C(21)	110·6 (0·4)
C(19)–C(20)–C(29)	110·7 (0·4)
C(19)–C(20)–C(30)	110·0 (0·3)
C(21)–C(20)–C(29)	107·8 (0·4)
C(21)–C(20)–C(30)	108·6 (0·4)
C(29)–C(20)–C(30)	109·1 (0·4)
C(20)–C(21)–C(22)	112·9 (0·3)
C(17)–C(22)–C(21)	115·5 (0·5)

By contrast the spiro ring must be under some strain. Of the non-bonded intramolecular contacts around this ring, the C(1)–C(25) and C(4)–C(25) distances (3·04 and 3·07 Å respectively) compare favourably with similar distances within the molecule *e.g.* C(13)–C(26) and C(15)–C(26) which are both 3·04 Å. The methyl–methyl distances C(23)–C(24) (3·14 Å) and C(23)–C(25) (3·97 Å) are also reasonable. However the C(24)–C(25) separation of 5·11 Å is substantially greater than C(28)–C(29) (4·64 Å) indicating that these methyl groups are probably being forced apart by proton interaction and could therefore account for the flexed configuration of the spiro ring.

The molecule is sited in the unit cell with the mean plane of the rings parallel to the *b* axis and its long dimension nearly parallel to **c** [Fig. 5(*a*) and (*b*)]. Its packing is closely similar to that of the steroids (Bernal, Crowfoot & Fankuchen, 1940) and falls into the structure type *a*212. In this class, *a*, the symbol 212 corresponds to two molecular thicknesses along **a** sin β, one molecule width along **b** and two molecule lengths along **c**. Van der Waals contacts are normal and in the range 3·75–3·95 Å.

This triterpane has been tentatively named 1(10 → 5) *abeo*-3β-methyl-24β-nor-25α-18-α-oleanane. It bears a close relationship to the oleanene series of natural triterpenes which are known to occur in plants. However no naturally occurring triterpene has been reported with a spiro *A*:*B* ring junction. Thus whilst it is possible that triterpenes have existed in early plant forms with this ring arrangement from which crude petroleum may have been derived, it is also possible for isomerization to have taken place during the process of petroleum formation. A more detailed discussion has already been published (Hills, Smith & Whitehead, 1968), describing the possible mechanisms whereby this molecular transformation could have arisen. Briefly it is suggested that processes, which are known to produce spiranization in steroid systems, may have occurred during the formation of petroleum to produce triterpane *E*. The transformation would include a 1:2 shift of the β(axial) methyl group at C(4) to the β(equatorial) position at C(3), at which position in natural triterpenes an oxygen group is often sited. Also included in transformation is the shift of the C(1)–C(10) bond to the C(5) position which implies the formation of one or more double bonds in the *A* or *B* rings, thus leaving the methyl group C(25) no longer at a ring junction.

The calculations were made upon the Elliott 803 computer using data reduction, structure factor and Fourier summation programs developed in these laboratories. The least-squares structure factor program was written by Dr G. Mair (Oxford University). The superposition maps were calculated on an IBM 7094 using programs provided by Dr C. E. Nordman.

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