

sulphide and 1.94 Å in tetraethyl diphosphine disulphide. The bond angle S-P-P' of 111.1° compares with 112° in dimethyl diphenyl diphosphine disulphide and 113° in tetraethyl diphosphine disulphide.

Table 6. Bond lengths and their standard deviations

Bond	Distance	σ
P—P'	2.21 Å	0.004 Å
S—P	1.95	0.002
P—C(1)	1.82	0.007
P—C(4)	1.82	0.007
C(1)—C(2)	1.52	0.011
C(3)—C(4)	1.51	0.010
C(2)—C(3)	1.52	0.015

Table 7. Bond angles and their standard deviations

	Angle	σ
S—P—C(1)	118.7°	0.3°
S—P—C(4)	116.5	0.3
S—P—P'	111.1	0.1
C(1)—P—P'	105.5	0.1
C(4)—P—P'	107.0	0.1
C(1)—P—C(4)	96.6	0.3
P—C(1)—C(2)	104.6	0.5
P—C(4)—C(3)	105.1	0.6
C(1)—C(2)—C(3)	108.5	0.8
C(2)—C(3)—C(4)	108.8	0.7

The bond lengths and angles in the ring show a regular arrangement. The P-C distances, both of 1.82 Å, are close to the values of 1.82 Å in dimethyl diphenyl diphosphine disulphide and of 1.82 and 1.84 Å in tetraethyl diphosphine disulphide. These values are in close agreement with the value of 1.84 Å obtained from the sum of Pauling's (1960) single bond covalent radii. The ring system is saturated and is consequently puck-

ered, and the bond angles round the carbon atoms are slightly less than the usual tetrahedral value. The inclusion of phosphorus in a heterocyclic ring causes considerable distortion of the tetrahedral environment round the phosphorus, and the bond angle C(1)-P-C(4) is 96.6°. It is surprising that this has no observable effect on the bond order of the P-P and P=S bonds. A large number of intermolecular contacts occur in the range 3.85–4.0 Å, but there are no intermolecular contacts below 3.85 Å except those involving hydrogen atoms.

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The Crystal Structure and Absolute Configuration of the *N*(*b*)-Methiodide of (–)-Kopsanone

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Crystals of the *N*(*b*)-methiodide of the indole alkaloid (–)-kopsanone, $[C_{21}H_{25}N_2O]^+I^-$, are orthorhombic with lattice translations $a = 13.98$, $b = 17.20$, $c = 7.67$ Å, space group $P2_12_12_1$, four formula units per unit cell. The crystal structure has been determined from 1800 three-dimensional X-ray intensity data, collected with an automatic four-circle diffractometer, the absolute configuration being established from the Cu $K\alpha$ anomalous scattering of the iodide ion. Refinement of positional and isotropic temperature factors was by full-matrix least-squares, giving convergence at $R = 0.08$. Hydrogen atom positions were not determined. The results confirm the molecular structure previously proposed on the basis of chemical and spectral data. The heptacyclic molecular structure has a cage-like aliphatic portion, with the piperidine ring *D* in the chair form. The conformation of the remainder of the molecule and of (–)-kopsanone itself follows from the interlocking nature of the ring fusions.

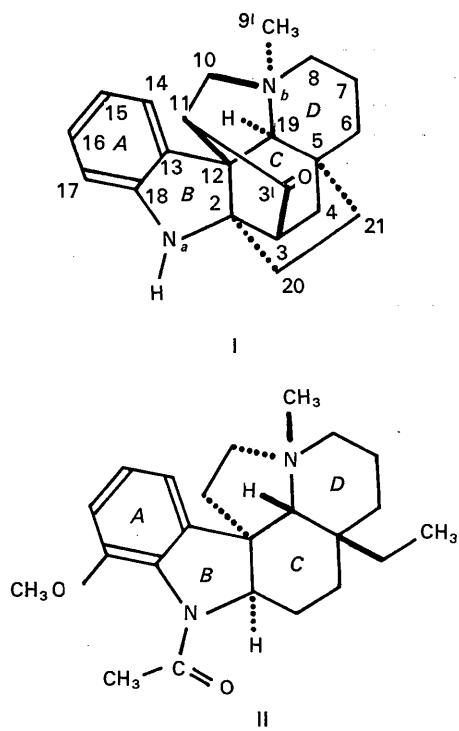
Introduction

Several families of indole alkaloids with similar molecular structures have been isolated from *Aspidosperma*,

Pleiocarpa, *Kopsia* and other genera. The chemistry of these alkaloids has been reviewed by Gilbert (1965). In considering their structural and biosynthetic relationships, (–)-kopsanone is important since it has been

isolated from two different genera (*Aspidosperma duckei* Hub., *A. macrocarpon* Mart, *Pleicarpa mutica* Benth; Ferreira Filho, Gilbert, Kitagawa, Paes Leme & Durham, 1966; Achenbach & Biemann, 1965) and possesses the heptacyclic skeleton of kopsine and other alkaloids which have been isolated from yet a third genus (*Kopsia*). Kopsanone has also been obtained by pyrolysis of kopsinic acid (Kump, Dugan & Schmid, 1966).

This paper concerns the crystal structure and absolute configuration of the *N*(*b*)-methiodide of (-)-kopsanone (I).* The results have already been reported briefly (Craven, Gilbert & Paes Leme, 1968).



Experimental

Crystals of kopsanone *N*(*b*)-methiodide were supplied by Drs Gilbert and Paes Leme of the Federal University of Rio de Janeiro, Brazil. The crystals are orthorhom-

* The atomic nomenclature in (I) conforms with Gilbert (1965).

bic with lattice parameters $a=13.98 \pm 0.005$, $b=17.20 \pm 0.05$ and $c=7.67 \pm 0.02$ Å, and space group $P2_12_12_1$. The crystal density of 1.62 g.cm $^{-3}$, measured by flota-

Table 2. *Atomic parameters with e.s.d.'s*

The positional parameters are expressed as fractions of the lattice translations.

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$	$B, \sigma(B)$
I	0.66765	0.78901	0.8632	3.69 Å ²
	0.00007	0.00006	0.0001	0.03
N(<i>a</i>)	0.4949	0.4393	0.479	3.4
	0.0010	0.0008	0.002	0.2
N(<i>b</i>)	0.5157	0.7084	0.403	2.6
	0.0008	0.0007	0.001	0.2
O	0.3504	0.5159	0.146	4.7
	0.0009	0.0007	0.002	0.2
C(2)	0.4541	0.5100	0.542	3.1
	0.0011	0.0009	0.002	0.3
C(3)	0.3575	0.5321	0.460	3.3
	0.0011	0.0009	0.002	0.3
C(3')	0.3899	0.5416	0.271	3.4
	0.0012	0.0009	0.002	0.3
C(4)	0.3252	0.6099	0.537	3.5
	0.0011	0.0009	0.002	0.3
C(5)	0.4060	0.6512	0.643	2.9
	0.0010	0.0008	0.002	0.2
C(6)	0.3821	0.7339	0.694	4.3
	0.0013	0.0010	0.003	0.3
C(7)	0.3769	0.7847	0.540	4.5
	0.0013	0.0011	0.003	0.3
C(8)	0.4761	0.7901	0.452	3.4
	0.0011	0.0009	0.002	0.3
C(9')	0.6191	0.7216	0.359	3.3
	0.0010	0.0008	0.002	0.3
C(10)	0.4677	0.6726	0.249	3.2
	0.0011	0.0009	0.002	0.3
C(11)	0.4841	0.5846	0.274	2.5
	0.0010	0.0008	0.002	0.2
C(12)	0.5214	0.5724	0.464	2.7
	0.0010	0.0008	0.002	0.2
C(13)	0.6161	0.5291	0.481	2.9
	0.0011	0.0008	0.002	0.3
C(14)	0.7116	0.5536	0.506	3.5
	0.0011	0.0009	0.002	0.3
C(15)	0.7847	0.4976	0.506	4.2
	0.0013	0.0011	0.003	0.3
C(16)	0.7651	0.4213	0.491	4.7
	0.0014	0.0011	0.003	0.4
C(17)	0.6668	0.3944	0.478	4.0
	0.0013	0.0009	0.002	0.3
C(18)	0.5977	0.4517	0.477	3.3
	0.0011	0.0009	0.002	0.3
C(19)	0.5070	0.6518	0.554	2.8
	0.0010	0.0008	0.002	0.2
C(20)	0.4251	0.6001	0.803	4.3
	0.0013	0.0011	0.003	0.3
C(21)	0.4476	0.5160	0.747	3.7
	0.0013	0.0010	0.002	0.3

Table 1. *Refinement criteria*

Criteria	1st refinement (enantiomer of true structure)	2nd refinement (true structure)
Standard deviation in an observation of unit weight	0.75	0.58
<i>R</i> index, all data	0.106	0.081
<i>R</i> index, omitting unobserved	0.102	0.077
Weighted <i>R</i> index, all data	0.131	0.100
Weighted <i>R</i> index, omitting unobserved	0.125	0.097

Table 3. Observed and calculated structure factors

The columns listed are k , $10|F_o|$, $10|F_c|$, $10A_c$, $10B_c$.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	4																																																					

Table 3 (cont.)

5 590 561 204- 522	13 417 427 121 410-	15 358 344 39- 341	1 172 200 45- 195	3 131 97 46 18-	3 267 292 55 286-
6 545 561 188 529-	14 47* 59 56 70	16 154 154 153- 13-	0 172 200 45- 195	4 716 704 642- 126-	4 578 652 638- 137-
7 563 572 187 555-	15 47* 405 246- 41-	17 150 153 153- 129-	1 172 200 45- 195	5 127 121 183 208	5 127 221 221 221
8 561 566 265-	16 242 242 246- 241-	18 148 124 43 116-	2 120 147 96- 112	6 175 147 21- 185	7 123 123 9- 114
9 334 361 103 346	17 148 124 43 116-	0 149 161 48- 153	3 160 184 178 56	7 300 280 6- 286-	8 612 649 636- 511
10 292 276 61 269-	18 124 116 45	1 519 463 227- 411	4 59 93 39- 84-	8 258 242 220 99-	9 80 38 35 15-
11 212 258 182- 183-	19 34* 33 4- 33	2 480 425 405 128-	L= 4 H= 0	9 210 189 51- 182	10 503 503 496 81
12 200 175 97- 145-	L= 3 H= 1	3 555 434 340- 437	C 290 314 208- 180-	10 449 455 455- 18-	11 174 192 47- 186
13 109 52 50 14-	C 199 197 64- 187	4 703 671 664- 130-	1 160 167 15- 150-	11 174 192 47- 186	12 45* 54 49- 22-
14 81 91 49- 57-	1 100 91 57- 575	5 333 541 229 220	2 167 167 166- 162-	12 505 496 496- 100-	13 171 173 123- 115-
15 88 120 44- 117-	2 777 746 735 276-	6 546 541 237 120	3 155 155 140 132- 46-	14 141 116 112- 27-	15 160 119 33- 114
16 134 160 -H- 160-	3 878 927 797- 473-	7 535 502 500 50	4 475 558 547- 11C-	14 384 340 337- 47-	15 160 119 33- 114
17 146 163 5- 133-	4 740 749 627- 331-	8 390 408 385- 129-	5 404 432 55- 428	15 96 110 92- 61	16 270 220 213 55
L= 2 H= 9	5 745 766 683- 348	9 331 309 309 7-	6 72 72 72 70-	19 15 257 213 189 95	L= 5 H= 1
0 79 44 43- 10-	10 6 757 822 760 315	10 420 453 419 172	7 418 430 54- 427-	0 621 604 85 598-	0 621 604 85 598-
1 82 81 70- 156-	7 5 748 778 716 11-	11 372 372 286 80	8 418 430 54- 427-	1 558 531 49- 630-	1 558 531 49- 630-
2 80 81 70- 156-	8 591 801 781 781	9 331 309 309 7-	9 401 418 54- 427-	2 386 392 146 533	2 386 392 146 533
3 616 599 594 74-	9 561 547 524 156-	13 252 258 4- 258-	10 577 575 563- 118-	3 643 690 451- 522	3 643 690 451- 522
4 170 118 89-	10 393 429 412 120	14 129 74 56- 48	11 198 206 19 205-	4 213 228 161- 138-	4 213 228 161- 138-
5 168 160 53- 160-	11 404 402 274- 294	15 199 197 8 196	12 647 618 664 130	5 319 332 285 171-	5 319 332 285 171-
6 214 191 11 19C-	12 128 110 167- 26-	16 177 154 154- 154	17 134 134 134- 134	6 375 366 263 254	6 375 366 263 254
7 183 166 88- 187-	13 298 280 144 240-	17 128 141 58- 128-	14 568 537 526- 108-	7 129 122 87- 86-	7 129 122 87- 86-
8 209 166 88- 130-	14 138 138 138- 138	18 154 154 154- 154	15 568 537 526- 108-	8 404 402 402 318-	8 404 402 402 318-
9 326 323 303- 303-	15 129 129 129 126	19 154 154 154- 154	16 568 537 526- 108-	9 347 347 347 336	9 347 347 347 336
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11 314 316 316- 34-	22 172 246 186 160-	23 683 642 36- 641	18 84 57 52- 52-	11 296 266 98 246-	11 472 478 91 470-
12 109 94 21- 21-	23 247 216 214- 35-	24 533 533 555- 170	19 135 135 135- 135	12 235 243 73- 231	12 235 243 73- 231
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14 96 65 2- 65-	15 338 340 309 160-	26 603 588 210- 160-	21 603 588 210- 160-	14 133 136 36 131-	14 133 136 36 131-
15 271 251 187- 187-	16 247 247 222 222	27 628 628 192 222	28 628 628 192 222	15 307 307 277 277	15 307 307 277 277
16 L= 2 H= 10-	29 675 168 901 901	29 455 455 455- 455-	30 446 436 436- 436-	16 157 157 157- 157	16 157 157 157- 157
L= 2 H= 10-	30 673 684 395 524-	31 455 455 455- 455-	32 446 436 436- 436-	17 157 157 157- 157	17 157 157 157- 157
0 153 174 174- 174	31 672 672 600- 301	33 411 393 293 293	34 325 341 244 238	C 419 423 415 84	L= 5 H= 2
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4 346 379 60- 60-	35 511 533 479 234-	38 409 409 288 380-	38 424 424 214 21-	3 714 704 694 272-	3 714 704 694 272-
5 670 681 62- 62-	36 511 533 479 234-	39 409 409 288 380-	39 424 424 214 21-	4 309 290 286 46-	4 309 290 286 46-
7 351 342 93 329-	40 511 533 479 234-	41 409 409 288 380-	41 424 424 214 21-	5 621 663 626- 217-	5 621 663 626- 217-
8 596 593 25 593-	42 511 533 479 234-	43 409 409 288 380-	43 424 424 214 21-	6 251 272 269- 37-	6 251 272 269- 37-
9 275 237 111- 250-	44 511 533 479 234-	45 409 409 288 380-	45 424 424 214 21-	7 132 101 1C- 21-	7 132 101 1C- 21-
10 305 274 111- 252-	46 511 533 479 234-	47 409 409 288 380-	47 424 424 214 21-	8 656 676 676 205-	8 656 676 676 205-
11 140 46 13- 13-	48 511 533 479 234-	49 409 409 288 380-	49 424 424 214 21-	9 155 133 98 90-	9 155 133 98 90-
12 81 96 28- 28-	50 511 533 479 234-	51 409 409 288 380-	51 424 424 214 21-	10 304 285 50- 280-	10 304 285 50- 280-
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15 72 107 16- 16-	56 511 533 479 234-	57 409 409 288 380-	57 424 424 214 21-	13 205 202 53- 195	13 205 202 53- 195
L= 2 H= 11-	58 511 533 479 234-	59 409 409 288 380-	60 424 424 214 21-	14 115 92 70 60-	14 115 92 70 60-
0 47* 42* 42* 37-	61 511 533 479 234-	62 409 409 288 380-	63 424 424 214 21-	15 67 85 74- 41-	15 67 85 74- 41-
1 156 197 72 139-	64 511 533 479 234-	65 409 409 288 380-	66 424 424 214 21-	16 120 93 55- 55-	16 120 93 55- 55-
2 78 67 8 66	L= 3 H= 4	67 409 409 288 380-	68 424 424 214 21-	17 241 305 84- 293	18 156 133 98 90-
3 392 411 28- 410-	69 409 409 288 380-	70 417 417 214 21-	71 241 305 84- 293	9 155 139 134- 39-	9 155 139 134- 39-
4 178 163 156- 177-	72 409 409 288 380-	73 417 417 214 21-	74 241 305 84- 293	10 304 285 50- 280-	10 304 285 50- 280-
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7 391 402 46- 46-	78 409 409 288 380-	79 417 417 214 21-	80 241 305 84- 293	12 440 427 39 425-	12 440 427 39 425-
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9 293 311 1C1 1C1	84 409 409 288 380-	85 417 417 214 21-	86 241 305 84- 293	14 1C1 1C1 46- 55-	14 1C1 1C1 46- 55-
10 127 89 89- 2-	87 387 375 110 110	88 417 417 214 21-	89 738 722 159 694-	15 244 222 6- 222-	15 244 222 6- 222-
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L= 2 H= 13-	94 387 375 110 110	95 409 409 288 380-	96 738 722 159 694-	L= 5 H= 5	L= 5 H= 5
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1 205 219 173 135	98 387 375 110 110	99 409 409 288 380-	100 738 722 159 694-	1 703 687 67- 674-	1 703 687 67- 674-
2 333 376 372 57	101 387 375 110 110	102 409 409 288 380-	103 738 722 159 694-	2 403 475 24- 240-	2 403 475 24- 240-
3 200 195 141- 135-	104 387 375 110 110	105 409 409 288 380-	106 738 722 159 694-	3 312 383 308 308-	3 312 383 308 308-
4 184 184 140- 135-	107 387 375 110 110	108 409 409 288 380-	109 738 722 159 694-	4 347 335 172- 287	4 347 335 172- 287
5 101 51 51 51	110 387 375 110 110	111 409 409 288 380-	112 738 722 159 694-	5 318 171 163 161- 70-	5 318 171 163 161- 70-
6 116 77 45 62- 62-	113 387 375 110 110	114 409 409 288 380-	115 738 722 159 694-	6 121 121 121 121- 70-	6 121 121 121 121- 70-
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9 68 130 125- 126-	122 387 375 110 110	123 409 409 288 380-	124 738 722 159 694-	9 136 136 136 136- 70-	9 136 136 136 136- 70-
10 226 213 199- 152-	125 387 375 110 110	126 409 409 288 380-	127 738 722 159 694-	10 137 137 137 137- 70-	10 137 137 137 137- 70-
11 85 85 85 85	127 387 375 110 110	128 409 409 288 380-	129 738 722 159 694-	11 147 147 147 147- 70-	11 147 147 147 147- 70-
12 244 307 304- 36-	130 387 375 110 110	131 409 409 288 380-	132 738 722 159 694-	12 244 443 443 443- 70-	12 244 443 443 443- 70-
13 240 446 447- 17-	125 387 375 110 110	133 409 409 288 380-	134 738 722 159 694-	13 312 383 308 308-	13 312 383 308 308-
14 245 446 447- 17-	126 387 375 110 110	135 409 409 288 380-	136 738 722 159 694-	14 244 242 242 242-	14 244 242 242 242-
15 223 253 252 19	127 387 375 110 110	137 409 409 288 380-	138 738 722 159 694-	15 222 202 198- 42-	15 222 202 198- 42-
0 44* 82 82 9	138 387 375 110 110	139 409 409 288 380-	140 738 722 159 694-	L= 5 H= 6	L= 5 H= 6
1 74 49 20- 44-	141 387 375 110 110	142 409 409 288 380-	143 738 722 159 694-	0 438 24 24- 23-	0 438 24 24- 23-
2 87 128 125- 126-	144 387 375 110 110	145 409 409 288 380-	146 738 722 159 694-	1 290 263 29 261	1 290 263 29 261
3 198 190 107- 157-	147 387 375 110 110	148 409 409 288 380-	149 738 722 159 694-	2 443 443 443 443-	2 443 443 443 443-
4 242 242 242 242-	150 387 375 110 110	151 409 409 288 380-	152 738 722 159 694-	3 312 383 308 308-	3 312 383 308 308-
5 216 246 246 246-	153 387 375 110 110	154 409 409 288 380-	155 738 722 159 694-		

Table 3 (cont.)

3	143	144	213	274	8	513	427	145	402	5	124	133	45	93
4	150	136	216	279	9	303	302	56	296	6	122	124	0	124
5	116	116	237	235	10	270	268	716	159	L =	6	H =	12	
6	211	214	117	165	11	146	147	127	135	0	116	115	12	35
7	147	147	162	12	43	63	61	12	1	1	107	108	106	
8	121	120	264	118	11	111	116	126	23	2	91	97	94	23
9	129	129	150	153	14	111	116	72	91	L =	1	H =	C	
10	ZCC	222	176	146	L =	6	H =	3		1	455	973	121	560
11	310	292	24	292	C	65	31	31	3	2	219	254	254	16
12	143	145	24	143	1	676	672	678	137	3	286	317	90	298
13	291	297	118	275	2	46	46	46	46	4	133	132	132	27
14	132	128	20	vrh	4	243	450	447	54	5	223	246	246	243
0	102	121	112	47	110	5	212	225	262	9	7	46*	78	16
1	132	150	17	149	6	141	125	43	117	8	150	183	181	26
2	268	270	215	162	7	161	137	136	15	9	243	257	28	251
3	334	340	207	187	8	236	245	57	238	10	60	38	35	16
4	103	147	44	44	9	455	427	418	89	11	340	307	78	297
5	146	146	120	120	10	146	146	120	120	12	38*	33	33	4
6	311	310	246	246	21	11	246	315	324	42	L =	7	H =	1
7	378	370	373	41	12	242	324	16	77	10	42*	38	17	34
8	178	194	50	33	13	355	347	317	141	1	16C	166	23	165
9	152	167	31	14	14	14	18	18	18	2	241	250	255	143
10	168	222	150	161	L =	6	H =	1		3	232	246	183	154
11	172	133	135	14	C	315	311	301	30	4	179	205	190	77
12	141	113	98	12	5	146	311	216	251	5	179	205	190	77
13	151	146	12	143	2	308	304	291	267	6	445	485	484	42
0	355	363	118	344	4	443	438	187	316	8	311	310	271	150
1	119	127	112	61	5	410	443	28	442	9	142	143	142	15
2	645	652	159	632	6	327	346	44	343	10	235	237	237	33
3	48*	33	33	33	7	308	308	68	68	11	160	147	135	96
4	148	186	12	186	8	410	410	9	117	12	340	340	38	10
5	132	163	145	74	9	219	208	153	141	L =	7	H =	2	
6	76	74	15	71	10	212	261	54	21	C	373	306	106	287
7	221	239	237	32	11	157	143	101	101	1	195	183	9	182
8	139	150	12	153	12	140	118	68	96	4	473	467	132	446
9	90	83	3	82	14	101	93	69	62	5	192	172	6	185
10	248	248	5	232	10	426	426	426	426	11	143	141	140	10
11	153	137	125	6	272	C	608	454	455	6	170	183	183	0
12	273	286	6	272	1	346	306	295	82	6	45	39	34	19
13	L =	5	H =	10	2	328	343	237	294	7	94	81	80	10
0	315	315	43	312	3	115	117	116	116	14	159	144	98	105
1	49	85	34	66	4	436	436	340	274	9	122	111	21	307
2	260	218	58	211	5	255	255	27	203	10	210	210	65	103
3	208	209	209	209	6	155	154	154	154	11	164	172	6	172
4	130	168	90	142	7	167	148	51	139	12	190	190	98	169
5	131	360	353	7C	8	178	186	156	152	L =	7	H =	3	
6	197	190	156	108	9	133	132	132	131	C	206	172	33	168
7	296	317	290	129	10	207	207	27	10	1	142	133	132	14
8	158	143	143	11	11	162	163	163	163	12	162	162	58	107
9	182	215	196	88	12	210	224	218	49	1	341	341	309	107
10	204	193	161	132	13	150	150	151	151	61	4	145	92	66
11	85	117	HC	85	L =	6	H =	6	54	5	349	380	370	95
0	272	304	55	299	1	100	100	156	98	6	129	121	51	110
1	379	396	1C	383	2	97	134	131	131	7	410	430	421	86
2	129	147	110	96	3	141	240	147	152	4	142	133	132	14
3	228	261	26	26	4	161	161	161	161	12	206	206	206	12
4	154	144	102	101	6	104	126	126	126	11	143	143	140	8
5	77	112	112	6	7	488	476	14C	455	12	376	377	1C	383
6	71	71	53	47	8	43	300	90	21	1	156	125	24	23
7	87	87	22	84	9	244	300	90	286	2	203	203	203	63
8	107	146	1C	1C	10	160	158	158	158	7	193	191	0	191
0	42*	18	3	16	12	157	148	140	44	4	250	267	26	266
1	70	67	69	68	13	53	35	31	16	5	178	171	114	127
2	206	210	29	19	L =	6	H =	7		6	430	43C	32	23
3	153	153	59	157	C	304	413	40G	1C1	7	141	134	132	14
4	200	248	232	88	1	303	304	277	12	8	172	161	161	131
5	72	76	67	76	7	244	244	244	244	7	43*	37	25	28
6	202	270	270	303	23	239	202	174	102	10	241	247	54	241
7	39*	146	61	61	8	245	308	308	2	11	130	195	65	140
0	42*	18	5	16	5	206	233	71	222	5	C	44*	40	16
1	106	122	33	117	6	108	105	73	73	1	181	105	105	105
2	178	222	123	105	7	233	220	1C	219	1	141	141	141	141
3	101	142	61	116	8	222	222	14C	142	4	177	176	176	133
4	145	180	65	160	9	146	172	142	142	4	317	326	298	133
5	124	124	44	116	10	189	186	184	32	5	167	185	185	9
6	93	126	126	6	4	270	294	67	281	C	110	108	6	108
7	567	606	12	594	5	162	196	39	192	1	510	509	127	493
8	47*	55	50	57	6	300	336	64	330	2	140	124	124	13
9	192	219	7C	200	7	178	182	74	154	1	237	237	237	147
10	120	104	9	120	8	202	202	114	146	4	181	212	161	161
11	125	125	44	141	9	149	148	48	188	5	52	50	32	36
12	185	171	165	143	10	168	169	119	120	6	64	84	75	39
13	40*	56	56	56	11	123	109	16	107	7	44*	45	10	44
14	130	140	136	36	87	C	44*	19	19	8	59	122	120	6
15	104	94	36	87	C	44*	19	19	5	9	173	175	28	172
0	631	543	124	124	1	315	345	325	325	1	141	141	141	141
1	319	344	342	283	3	204	217	174	174	C	193	253	78	241
2	447	467	462	464	4	165	139	10	139	1	1C7	83	31	77
3	394	447	316	316	5	115	95	94	15	2	235	203	181	91
4	337	375	372	42	6	155	163	51	154	3	43*	37	32	27
5	52	241	18	240	7	61	61	31	31	4	242	230	225	47
6	209	193	164	164	8	147	180	168	163	6	213	237	234	35
7	197	193	125	145	9	109	28	20	19	7	161	158	150	48
8	186	199	153	124	10	121	110	24	1C8	9	161	158	150	48
9	197	191	125	145	0	.79	28	20	19	7	161	158	150	48
10	229	234	222	75	1	143	174	75	75	7	290	288	284	48
11	197	190	149	149	2	163	163	147	147	0	167	208	204	43
12	293	304	292	83	2	163	163	147	147	1	1C8	141	126	126
13	226	270	270	13	2	157	247	179	176	1	197	142	126	127
14	209	260	294	24	4	233	268	68	260	2	283	293	47	279

$$\sigma(F) = |F_{\min}| + 0.07|F|,$$

where $|F_{\min}|$ is the average value of the structure amplitude assigned to unobservably weak reflections.

The criteria of the refinement process are shown in Table 1. The first refinement converged after three cycles of least squares. The atomic positional parameters were then inverted with respect to the crystallographic origin, and the resulting enantiomeric structural parameters were then refined with an additional two cycles. The improved agreement between calculated and observed structure factors in the second refinement suggests that these parameters, when referred to a right-handed set of crystal axes, correspond to the correct absolute configuration. This absolute configuration was confirmed by comparison of the observed and calculated intensity differences [$I(hkl) - I(\bar{h}\bar{k}\bar{l})$] as shown in Table 4. The final atomic parameters with e.s.d.'s from the second refinement are listed in Table 2. The corresponding observed and calculated structure factors are listed in Table 3. A three-dimensional electron density difference map was calculated, with the use of the atomic parameters shown in Table 2. The most prominent features in this map were at the iodine atom position. These could be interpreted as the effects of anisotropic thermal motion of the iodine atom with perhaps some contribution from systematic errors in the intensity data arising from progressive radiation damage in the crystal. Hydrogen atom positions were not determined.

Table 4. Determination of absolute configuration

h	k	l	$(I_{hkl} - I_{\bar{h}\bar{k}\bar{l}})/I_{hkl}$
1	1	1	calc.* +0.27
1	3	3	-0.17
9	1	2	+0.02
			obs. +0.22 -0.25 +0.02

* These values are based on the atomic parameters listed in Table 2, referred to a right-handed crystal axial system.

Description of the structure

The bond lengths and angles within the molecule are listed in Table 5. These may be referred to the molecular framework shown in Fig. 1. Calculation of best least-squares planes (Table 6) shows that both rings *A* and *B* of the dihydroindole moiety are distorted from planarity as a result of the steric requirements of fusion with the cage-like aliphatic part of the molecule. In ring *A*, only atom C(13) is significantly out of plane. The five-membered ring *B*, containing nitrogen atom N(*a*) is approximately in the envelope form, with atom C(2) at the flap position. A similar conformation is found for the cyclopentanone ring, in which the carbon atom C(2) is again at the flap position. The atoms of the carbonyl group and the two adjacent carbon atoms are coplanar (Table 6). The ring junctions in this molecule are all *cisoid*. Furthermore, all rings share three edges with other rings, except for rings *B* and *D*, which

share only two, and ring *A*, which shares only one. The molecule is thus rigid, except for ring *D*, which could reasonably be expected to be in either the chair or skew-boat conformation (Eliel, Allinger, Angyal & Morrison, 1965). The chair conformation is observed.

The packing in the crystal structure is shown in Fig. 2. A notable feature is the overlap of the aromatic rings *A*, which lie close to the planes $z=0, \frac{1}{2}$. It might be supposed that this would be an attractive interaction of some importance in the crystal structure. However, the separation of aromatic ring planes ($c/2$ or 3.83 \AA) is considerably greater than the van der Waals separation (3.4 \AA) as a result of the packing requirements of the bulky cage-like aliphatic portion of the molecule. Observed intermolecular distances are listed in Table 7.

Each iodide ion is enclosed so that it is within a 5 \AA distance of twenty-seven atoms from eight different molecular ions. The shortest of these distances (3.65 \AA) is to a nitrogen atom N(*a*) along a line which is approximately in the expected direction for the N(*a*)-H bond. This distance is considerably shorter than the sum (4.3 \AA) of the N-H bond length (assuming a value of 0.9 \AA), the van der Waals radius for hydrogen (1.2 \AA), and the ionic radius for iodine (2.2 \AA). Thus, even allowing for some non-collinearity of the atoms N(*a*)-H...I⁻, there is evidence of an attractive interaction, which might be called a hydrogen bond. In the crystal structures of the *N*(*b*)-methiodide of the alkaloid cleavamine (Cameron & Trotter, 1964) and also in hexamminecobalt(III) triiodide (Barnet, Craven, Freeman, Kime & Ibers, 1966) there are even shorter N-H...I⁻ distances (3.41 , 3.46 \AA , respectively) although in these cases also, the hydrogen atom positions were not experimentally determined.

In kopsanone methiodide, there are no significant dipole-dipole interactions between carbonyl groups similar to those described by Bolton (1964). The C...O

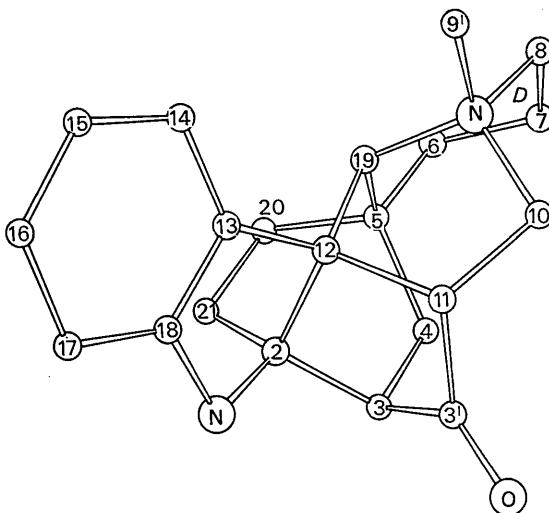


Fig. 1. Molecular framework of the kopsanone ion, showing the absolute configuration.

Table 5(a). Bond lengths and angles

The average e.s.d.'s in bond lengths and angles are 0.02 Å and 1.5° respectively.

(a) Bond lengths					
N(a)-C(2)	1.43 Å	C(5)-C(19)	1.57 Å	C(12)-C(13)	1.52 Å
C(2)-C(3)	1.54	C(5)-C(20)	1.53	C(12)-C(19)	1.54
C(2)-C(12)	1.55	C(6)-C(7)	1.47	C(13)-C(14)	1.41
C(2)-C(21)	1.58	C(7)-C(8)	1.55	C(13)-C(18)	1.36
C(3)-C(3')	1.53	C(8)-N(b)	1.56	C(14)-C(15)	1.40
C(3)-C(4)	1.53	N(b)-C(9')	1.50	C(15)-C(16)	1.35
C(3')-O	1.19	N(b)-C(10)	1.49	C(16)-C(17)	1.45
C(3')-C(11)	1.51	N(b)-C(19)	1.52	C(17)-C(18)	1.38
C(4)-C(5)	1.56	C(10)-C(11)	1.54	C(18)-N(a)	1.45
C(5)-C(6)	1.51	C(11)-C(12)	1.56	C(20)-C(21)	1.54

Table 5(b) Bond lengths averaged according to bond type

Trigonally and tetrahedrally bonded atoms are denoted by 'trig' and 'tetr'.

Type	No. of bonds	Average bond length	R.m.s. deviation
C(tetr)-C(tetr)	14	1.54 Å	0.007 Å
C(tetr)-C(trig)	3	1.52	0.005
C(trig)-C(trig)	6	1.40	0.015
N(tetr)-C(tetr)	4	1.52	0.014

(c) Bond angles

C(18)-N(a)-C(2)	106°	C(6)-C(5)-C(19)	108°	C(11)-C(12)-C(19)	105°
N(a)-C(2)-C(3)	115	C(6)-C(5)-C(20)	112	C(2)-C(12)-C(13)	99
N(a)-C(2)-C(12)	103	C(19)-C(5)-C(20)	101	C(2)-C(12)-C(19)	111
N(a)-C(2)-C(21)	115	C(5)-C(6)-C(7)	111	C(13)-C(12)-C(19)	120
C(3)-C(2)-C(12)	102	C(6)-C(7)-C(8)	110	C(12)-C(13)-C(14)	134
C(3)-C(2)-C(21)	110	N(b)-C(8)-C(7)	112	C(12)-C(13)-C(18)	108
C(12)-C(2)-C(21)	112	C(8)-N(b)-C(9')	105	C(14)-C(13)-C(18)	118
C(2)-C(3)-C(3')	99	C(8)-N(b)-C(10)	114	C(13)-C(14)-C(15)	119
C(2)-C(3)-C(4)	108	C(8)-N(b)-C(19)	112	C(14)-C(15)-C(16)	121
C(3)-C(3)-C(4)	112	C(9')-N(b)-C(10)	109	C(15)-C(16)-C(17)	121
C(3)-C(3')-C(11)	107	C(9')-N(b)-C(19)	110	C(16)-C(17)-C(18)	116
C(3)-C(3')-O	126	C(10)-N(b)-C(19)	108	C(17)-C(18)-C(13)	124
C(11)-C(3')-O	127	N(b)-C(10)-C(11)	104	C(17)-C(18)-N(a)	121
C(3)-C(4)-C(5)	113	C(10)-C(11)-C(3')	110	C(13)-C(18)-N(a)	109
C(4)-C(5)-C(6)	114	C(10)-C(11)-C(12)	107	C(5)-C(19)-N(b)	114
C(4)-C(5)-C(19)	115	C(3')-C(11)-C(12)	104	C(5)-C(19)-C(12)	108
C(4)-C(5)-C(20)	106	C(11)-C(12)-C(2)	105	N(b)-C(19)-C(12)	103
		C(11)-C(12)-C(13)	116	C(5)-C(20)-C(21)	110
				C(20)-C(21)-C(2)	111

Table 6. Best least-squares planes

(i) Equations of the planes

The equations of these planes are in the form $AX+BY+CZ=D$, referred to the crystallographic axes, with X , Y , Z in Å units.

Plane 1: atoms of the benzene ring, except for C(13).

Plane 2: atoms of the carbonyl group, with adjacent atoms.

Plane	A	B	C	D
1	-0.06137	-0.06663	0.99588	2.61843
2	-0.50219	0.86129	-0.07732	5.10548

(ii) Distances of atoms from the planes

For each plane, column (a) lists distances from the plane of atoms which form the plane, and column (b) lists distances from the plane of atoms which do not form the plane. The e.s.d. in these distances is approximately 0.015 Å.

Plane (1)

(a)	(b)
C(14) -0.00 Å	N(a) 0.11 Å
C(15) 0.01	C(13) -0.08
C(16) -0.01	C(12) -0.18
C(17) 0.01	C(2) 0.54
C(18) -0.00	

Plane (2)

(a)	(b)
C(11) -0.01 Å	C(12) -0.56 Å
C(3') 0.02	C(2) -1.06
C(3) -0.01	
O -0.01	

intermolecular distance is long (4.53 Å), although in Fig. 2 the projected distance is deceptively short.

Discussion

The present crystal structure determination of the *N*(*b*)-methiodide confirms the molecular structure for (-)-kopsanone determined from chemical and spectral data (Ferreira Filho *et al.*, 1966; Kump, *et al.*, 1966) and the absolute configuration which was proposed on the basis of a chemical correlation with minovincine (Kump *et al.*, 1966).

The determination of absolute configuration is of more than usual importance for *Aspidosperma* and related alkaloids, because of the existence of naturally occurring enantiomeric molecular structures. Quebrachamine and pyrrolidine are among those *Aspidosperma* alkaloids for which enantiomers have been isolated from different plant sources (see references given by Djerassi, Archer, George, Gilbert & Antonaccio, 1961). Wenkert (1962) has suggested mechanisms for indole alkaloid biosynthesis that involve a non-asymmetric intermediate. Although this can explain the observed enantiomerism, the conditions which result in the occurrence of a particular enantiomer in a particular plant are not yet understood.

From chemical and optical rotatory dispersion data, assignments of absolute configuration have been made (Klyne, Swan, Bycroft, Schumann & Schmid, 1965), which may be extended to include most of the known *Aspidosperma* and related alkaloids. However, except

in the present case and in the recent work on the *N*(*b*)-methiodide of (-)-aspidospermine* (Craven & Zacharias, 1968), the X-ray anomalous scattering method has not previously been used to determine the absolute configuration of an alkaloid closely related to the naturally occurring *Aspidosperma* series. These X-ray results confirm the previous assignments in showing that, except at carbon atom C(2), the *N*(*b*)-methiodides of (-)-kopsanone (I) and (-)-aspidospermine (II) have opposite configurations at each of the five asymmetric centers which they have in common. The difference in absolute configuration at carbon atom C(2) in (-)-kopsanone with respect to (+)-aspidospermine indicates that these compounds may be related by the cyclization at atom C(2) of the ethyl substituents at carbon atom C(5) in the latter compound.

Smith & Wrobel (1960) have given some evidence that the conformation of aspidospermine is different from that which is observed in the crystal structure of the *N*(*b*)-methiodide (Mills & Nyburg, 1960) and that the *N*-methylation reaction of aspidospermine involves an 'umbrella'-type inversion of configuration about the nitrogen atom *N*(*b*). Such behaviour is unlikely in the case of kopsanone because of the rigidity of the cage-like aliphatic portion of the molecule. Three of the bonds in the piperidine ring *D* are locked in positions so that flexing of this ring in the process of nitrogen atom inversion involves considerable angular strain. The de-

* The crystal structure was reported by Mills & Nyburg (1960), but the absolute configuration was not determined.

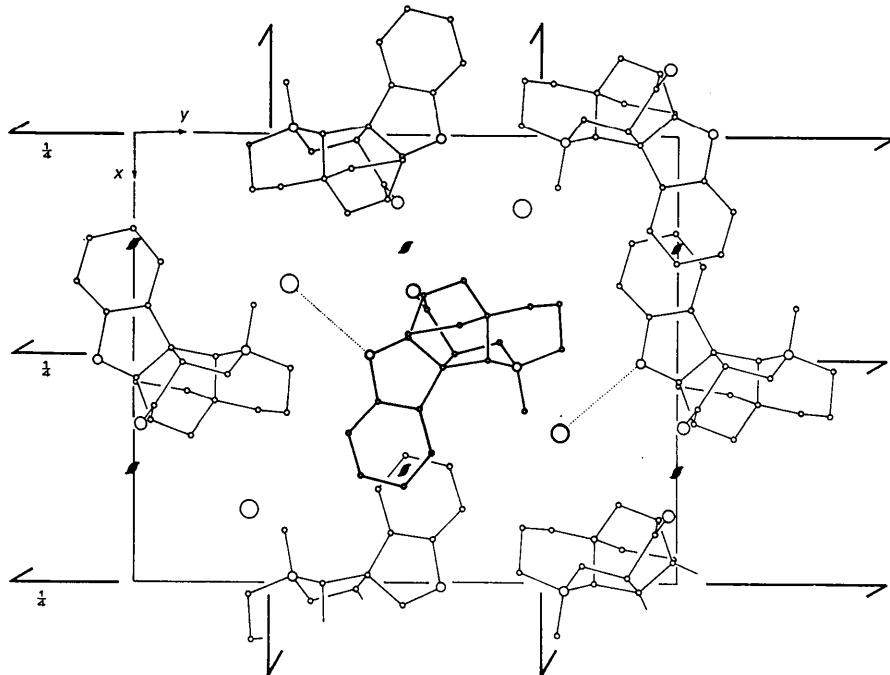


Fig. 2. The crystal structure of kopsanone *N*(*b*)-methiodide. The positive sense of the crystal axis *c* is towards the viewer. The atomic parameters of Table 2 refer to the molecule in the center. The presumed *N*(*a*)H · · · I⁻ hydrogen bonds are shown as dotted lines.

Table 7. Intermolecular distances

The interatomic distances listed include all those which are less than 0.2 Å in excess of the sum of the appropriate ionic or van der Waals radii (2.2 Å for I⁻, 2.0 Å for tetrahedrally bonded carbon, 1.7 Å for trigonally bonded carbon, 1.4 Å for oxygen; Pauling, 1960). Distances which are long by this criterion are indicated by *.

Subscripts (*a*, *b*, *c* ...) indicate that the right-hand member of each pair of atoms is related to the atom listed in Table 2 by one of the following symmetry operations:

<i>a</i> :	1 - <i>x</i>	$\frac{1}{2} + y$	$\frac{3}{2} - z$	<i>f</i> :	$\frac{1}{2} - x$	1 - <i>y</i>	$\frac{1}{2} + z$	
<i>b</i> :	$\frac{1}{2} + x$	$\frac{3}{2} - y$	$\frac{1}{2} - z$	<i>g</i> :	- $\frac{1}{2} + x$	$\frac{3}{2} - y$	1 - <i>z</i>	
<i>c</i> :	<i>x</i>	<i>y</i>	$1 + z$	<i>h</i> :	<i>x</i>	<i>y</i>	$-1 + z$	
<i>d</i> :	$\frac{3}{2} - x$	1 - <i>y</i>	$\frac{1}{2} + z$	<i>i</i> :	$\frac{3}{2} - x$	1 - <i>y</i>	$-\frac{1}{2} + z$	
<i>e</i> :	1 - <i>x</i>	$-\frac{1}{2} + y$	$\frac{3}{2} - z$	<i>j</i> :	$\frac{1}{2} - x$	1 - <i>y</i>	$-\frac{1}{2} + z$	
I ⁻ N(<i>a</i>) _{<i>a</i>}	3.65 Å (hydrogen bond)		N(<i>a</i>)	... I ⁻	3.65 (hydrogen bond)		
 C(3) _{<i>a</i>}	4.40		C(2)	... I _{<i>e</i>}	4.22*		
 C(4) _{<i>b</i>}	4.16		C(3)	... O _{<i>f</i>}	3.34*		
 C(6)	4.30			... I _{<i>e</i>} ⁻	4.40		
 C(8)	4.14		C(3')	... C(20) _{<i>h</i>}	3.76		
 N(<i>b</i>)	4.34			... C(21) _{<i>h</i>}	4.12*		
 C(9') _{<i>c</i>}	4.03		C(4)	... O _{<i>f</i>}	3.38		
 C(9')	4.09			... I _{<i>g</i>} ⁻	4.16		
 C(10) _{<i>b</i>}	4.33		C(6)	... C(9') _{<i>g</i>}	3.78		
 C(16) _{<i>a</i>}	3.86			... C(17) _{<i>a</i>}	3.80		
 C(17) _{<i>a</i>}	4.01			... I ⁻	4.30		
 C(19)	4.03		C(7)	... C(9') _{<i>g</i>}	3.69		
 C(21) _{<i>a</i>}	4.31			... C(14) _{<i>g</i>}	3.63		
C(7)	... C(15) _{<i>g</i>}	3.98		C(16)	... C(14) _{<i>t</i>}	3.76*		
C(8)	... I ⁻	4.14			... C(14) _{<i>a</i>}	3.99*		
N(<i>b</i>)	... I ⁻	4.34			... C(15) _{<i>t</i>}	4.03*		
C(9)	... C(6) _{<i>b</i>}	3.78			... I _{<i>t</i>} ⁻	3.86		
	... C(7) _{<i>b</i>}	3.69		C(17)	... C(6) _{<i>e</i>}	3.79		
	... I _{<i>h</i>} ⁻	4.03			... I _{<i>t</i>} ⁻	4.01		
	... I ⁻	4.09		C(18)	... C(15) _{<i>t</i>}	4.06*		
C(10)	... C(20) _{<i>h</i>}	3.69			C(19)	... C(16) _{<i>a</i>}	4.79*	
	... I _{<i>g</i>} ⁻	4.33			... I ⁻	4.03		
C(11)	... C(20) _{<i>h</i>}	3.71		C(20)	... C(3') _{<i>c</i>}	3.76		
	... C(21) _{<i>h</i>}	4.24*			... C(10) _{<i>c</i>}	3.69		
C(13)	... C(15) _{<i>a</i>}	3.92*			... C(11) _{<i>c</i>}	3.71		
C(14)	... C(7) _{<i>b</i>}	3.63			... O _{<i>c</i>}	3.18		
	... C(15) _{<i>t</i>}	3.93*		C(21)	... C(11) _{<i>c</i>}	4.24*		
	... C(15) _{<i>d</i>}	3.94*			... O _{<i>c</i>}	3.35		
	... C(16) _{<i>d</i>}	3.76*		O	... C(3) _{<i>j</i>}	3.34*		
C(15)	... C(13) _{<i>a</i>}	3.92*			... C(4) _{<i>j</i>}	3.38		
	... C(14) _{<i>t</i>}	3.94*			... C(20) _{<i>h</i>}	3.18		
	... C(14) _{<i>d</i>}	3.93*			... C(21) _{<i>h</i>}	3.35		
	... C(15) _{<i>t</i>}	3.96*						
	... C(15) _{<i>d</i>}	3.96*						
	... C(16) _{<i>d</i>}	4.03*						

tailed conformation of (-)-kopsanone thus follows from that of the *N*(*b*)-methiodide, as described in the previous section and as shown in Fig. 1.

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