Syntheses of Acridone and Carbazole Alkaloids involving Pyridine-catalysed Chromen Formation: Crystal and Molecular Structure of Dibromocannibicyclol and its Bearing on the Structures of the ' Cyclol ' Alkaloids

By **Wikramasinghe M. Bandaranayake, Michael J. Begley, Brian O. Brown, David G. Clarke, Leslie Crombie** * and **Donald A. Whiting,*** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

The pyrano[2.3-*c*]acridine alkaloid acronycine (2) and its [2.3-*b*] isomer (6) have been synthesised *via* pyridine-catalysed condensation of 1.3-dihydroxyacridone with 4.4-dimethoxy-2-methylbutan-2-ol: mono- and bis-prenylogues have been prepared similarly by aldehyde condensations. The 3-(4-methylpent-3-enyl)pyrano-[2.3-*c*]acridone (9) cyclises further to give products with one (14) or two [(13) and (37)] further rings. The acridone anils (15) and (16) have also been encountered.

The structure of cannabicyclol (the ' type ' structure of the ' cyclol ' system) has been elucidated by *X*-ray analysis of its dibromo-derivative. Dibromocannabicyclol formed triclinic crystals with petroleum of crystallisation. space group $P\bar{1}$, a = 9·14(3). b = 10·20(3), c = 15·51(4) Å. α = 112·9(4). β = 87·2(6). γ = 116·0(4)°, Z = 2. By using 2383 observed reflections the structure was solved by the heavy atom procedure and refined to R = 7·6%. In the light of the results. the structures of the carbazole alkaloids bicyclomahanimbine and bicyclomahanimbicine were revised to the 11.12-methanocyclopenta[5,6]pyrano[3.2-*a*]carbazole systems (35) and (36). Acid-catalysed cyclisation of (±)-mahanimbine (25) yields cyclomahanimbine (27) and its isomer (29): revision of structure (28) for curryanin to (27) is proposed.

MONO- AND HEMI-TERPENOID attachments are common structural features of natural phenolic meroterpenes. A variety of such units may be introduced [1-4] into phenols by pyridine-catalysed condensation with citral, 3-methylcrotonaldehyde, their dimethyl acetals, or 4,4-dimethoxy-2-methylbutan-2-ol (1).[4] Syntheses of 2,2-dimethylchromens (*e.g.* jacareubin,[4] lonchocarpin,[4] and evodionol methyl ether [4]) and of 2-methyl-2-(4-methylpent-3-enyl)chromens (*e.g.* cannabichromen [2] and flemingin A-, B-, and C-methyl ethers [3]) have been achieved in this way. Further, the monoterpenoid chromens may be modified to provide polycyclic natural compounds such as deoxybruceol,[1] cannabicyclol,[2] rubranine,[4] and many relatives.

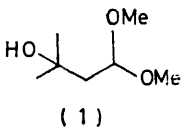
In this paper we describe further applications of this method to prepare alkaloids including acronycine (an anti-tumour acridone constituent of *Acronychia bauerii* Schott) and some of its isomers and prenylogues, together with carbazoles from *Murraya koenigii* Spreng. Certain structural revisions are made, and since some of the structures are dependent on the correctness of our earlier revision of the structure of cannabicyclol,[2] details of the *X*-ray structure determination of dibromocannabicyclol are included.

Acronycine (acronine) (2), one of several acridones [5] in the bark of *A. bauerii* has a sufficiently broad-spectrum anti-tumour activity to warrant clinical trials.[6] Three related syntheses have been reported [7] but all are lengthy and proceed in poor yield. We have found that condensation of 1,3-dihydroxyacridone (3) with the hydroxy-acetal (1) in pyridine at 150° gives a mixture of the linear and angular chromens (4) and (5) (*ca.* 1 : 3). Crystallisation afforded the major angular isomer, de-*N*-methylnoracronycine, which has been found [5g] in the root-bark of *Glycosmis pentaphylla* (Retz.) Correa: direct comparison established the identity of the specimens. Methylation then gave acronycine (2), m.p. 175—176° (24% from 1,3-dihydroxyacridone), identical with a natural specimen.[8] The structure of acronycine is firmly based on chemical and spectroscopic studies [5] and the angular chromen attachment is confirmed by the results of *X*-ray crystallographic studies on a bromodihydroacronycine.[7] The minor linear product, isoacronycine (6) was obtained together with noracronycine (7) by preparative layer chromatography

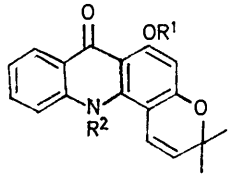
[1] L. Crombie and R. Ponsford, *J. Chem. Soc.* (*C*), 1971, 788.
[2] L. Crombie and R. Ponsford, *J. Chem. Soc.* (*C*), 1971, 796.
[3] W. M. Bandaranayake, L. Crombie, and D. A. Whiting, *J. Chem. Soc.* (*C*), 1971, 804.
[4] W. M. Bandaranayake, L. Crombie, and D. A. Whiting, *J. Chem. Soc.* (*C*), 1971, 811.
[5] (*a*) G. H. Hughes, F. N. Lahey, J. R. Price, and L. J. Webb, *Nature*, 1948, **162**, 223; (*b*) F. N. Lahey and W. C. Thomas, *Austral. J. Sci. Res.*, **A2**, 1949, 423; (*c*) R. D. Brown, L. J. Drummond, F. N. Lahey, and W. C. Thomas, *ibid.*, 1949, 622; (*d*) L. J. Drummond and F. N. Lahey, *ibid.*, 1949, 630; (*e*) R. D. Brown and F. N. Lahey, *ibid.*, 1950, 593; (*f*) P. L. Macdonald and A. V. Robertson, *Austral. J. Chem.*, 1966, **19**, 275; (*g*) T. R. Govindachari, B. R. Pai, and P. S. Subramaniam, *Tetrahedron*, 1966, **22**, 3245.
[6] G. H. Svoboda, G. A. Poore, P. J. Simpson, and G. B. Boder, *J. Pharm. Sci.*, 1966, **55**, 758; F. E. Gainer and W. Arnett, *ibid.*, 1969, **58**, 1548.
[7] J. R. Beck, R. Kwock, R. N. Booher, A. C. Brown, L. F. Patterson, P. Pranc, B. Rockey, and A. Pohland, *J. Amer. Chem. Soc.*, 1968, **90**, 4706.
[8] Preliminary communication, W. M. Bandaranayake, L. Crombie, and D. A. Whiting, *Chem. Comm.*, 1969, 970.

(p.l.c.) of the whole chromenylation product after methylation. Another satisfactory synthesis of acronycine involving rearrangement of a prop-2-ynyl ether of 1,3-dihydroxyacridone has been devised.[9]

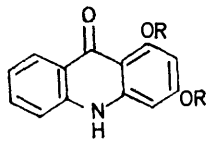
Our method can be developed further to yield prenylogues of pharmacological interest. The acridone (3) (purified *via* its diacetate) with citral and pyridine at 120° gave four compounds, isolated by p.l.c. The major (38%) was the angular chromen (9), readily



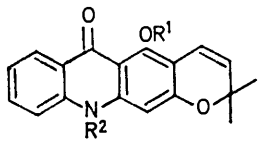
(1)



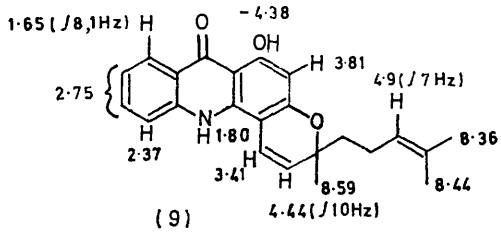
(2) $R^1 = R^2 = Me$
(5) $R^1 = R^2 = H$
(7) $R^1 = H, R^2 = Me$



(3) R = H
(8) R = Ac



(4) $R^1 = R^2 = H$
(6) $R^1 = R^2 = Me$



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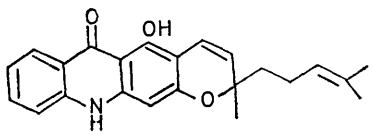
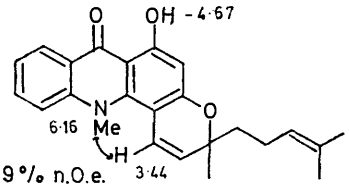


(10)



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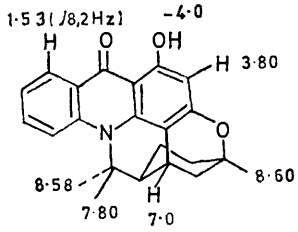

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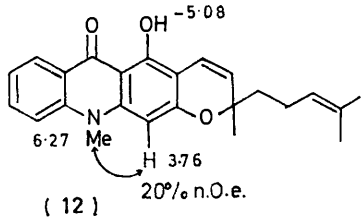


(12)

characterised by the n.m.r. spectrum (see illustrated formula). Also isolated was the linear isomer (10) (19%). The two chromens could be distinguished by the photometric Gibbs' test and by nuclear Overhauser effects in the *N*-methylated chromens (11) and (12) obtained by partial methylation. Both *N*-methyl derivatives gave positive reactions with iron(III) chloride. The angular compound (11) showed an *N*-methyl signal at τ 6·16 and the integrated intensity of this showed a reproducible selective increase of 9% on irradiation at the frequency corresponding to the nearest olefinic proton of the chromen ring. In contrast, the linear form (12) showed 20% increase in the *N*-methyl absorption only on irradiation at the frequency corresponding to the aromatic singlet at τ 3·76.

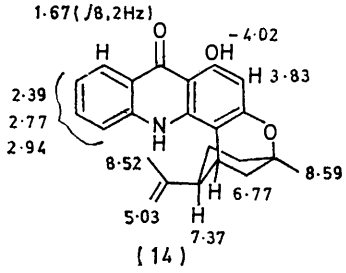
The third compound isolated proved to be the hexacyclic ' citrylideneacridone ' (13) (6%) recognised by spectral resemblances to similar, but fully oxygenated, heterocycles.[1-3] The n.m.r. spectrum showed a benzylic proton signal (τ 7·0), but no signals corresponding to olefinic protons; i.r. data confirmed the presence of the chelated carbonyl system (1635 cm^{-1}), but N–H bands were absent. U.v. data are consistent with an acridone structure without extended conjugation. This compound could also be obtained (30%) by heating the angular chromen (9) in pyridine at 180° (48 h): a parallel conversion is that of cannabichromen into citrylidenecannabis.[2] The fourth product was assigned the isopropenyl structure (14): again fully oxygenated

[9] J. Hlubucek, E. Ritchie, and W. C. Taylor, *Chem. and Ind.*, 1969, 1809; *Austral. J. Chem.*, 1970, **23**, 1881.

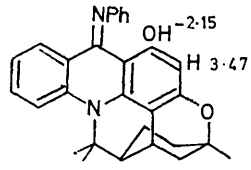
analogues are available in the cannabis series.[2] N.m.r. data are shown on the illustrated formula (14) and the acridone nucleus has an N–H i.r. absorption (3400 cm^{-1}). The isopropenyl compound (14) can be prepared by acid-catalysed ring opening of the citrylideneacridone (13) and by acid-catalysed cyclisation of the chromen (9). The former conversion shows that the isopropenyl group in (14) is equatorial.

Differences in product composition were found when purified and unpurified 1,3-dihydroxyacridone were employed in the reaction with citral. Use of the latter led to two additional products, both $C_{29}H_{28}N_2O_2$. Spectroscopic comparison revealed considerable similarities to the acridones (13) and (14), but the n.m.r. spectrum of each displayed signals due to five additional aromatic protons. These facts lead to structures (15) and (16) for the new products, *i.e.* they are the anils of the acridones. Other n.m.r. data accord with this view; the influence of the phenylimino-group is apparent in the chemical shifts of the hydroxy-group and the adjacent aromatic protons. The anils (15) and (16) show distinctive u.v. absorptions at 423 and 430 nm which differentiate them from the parent acridones. The unpurified 1,3-dihydroxyacridone does not contain unchanged anthranilic acid, or aniline, and the most likely explanation of the origin of (15) and (16) is that the 1,3-dihydroxyacridone, before purification, is contaminated with its own anil: this has not, however, been firmly established.

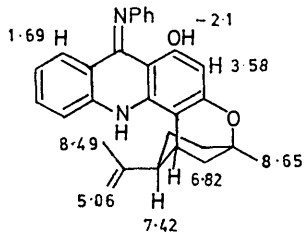
Farnesal * has been used for elaboration of chromens,[3] and its employment in the reaction with 1,3-dihydroxyacridone at 150° in the presence of pyridine gave the angular (35%; m.p. 174—175°) and linear (2%; m.p. 229—230°) chromens (17) and (18). These bis-prenylogues of (5) and (4) were characterised by n.m.r. data and the orientation of substituents was indicated by the photometric Gibbs' reaction. Comparison of their u.v. data with those for the mono-prenylogues (9) and (10) (see Figure 1), shows that the same differences occur between the pairs of curves and gives a useful additional criterion for orientation. A third isomeric product (19) was found in the reaction mixture, and spectral data are characteristic of the ' citrylidene ' type. Further, n.m.r. data define the stereochemistry at the carbon atom attached to nitrogen as shown. The *N*-*C*-methyl group which resonates at lower field in the acridone (13) (nearly coplanar with the aromatic ring) is replaced by the 4-methylpent-3-enyl group in (19).



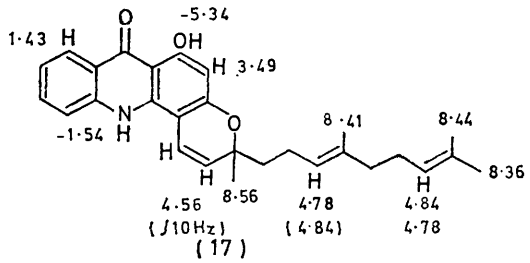
(14)



(15)



(16)



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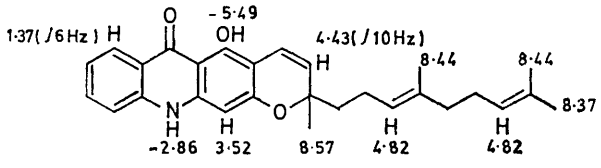
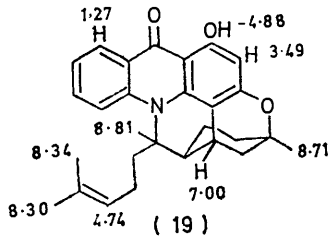


(18)



(19)

* A mixture of all-*trans*- and *cis*-2,*trans*-6-stereoisomers.

Implications of this stereochemical result are developed elsewhere.[10]

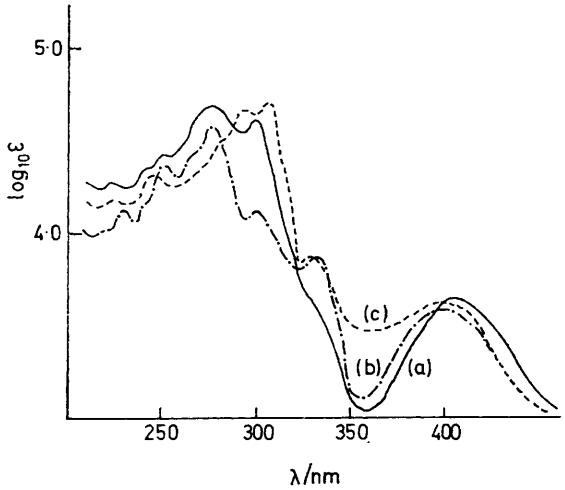
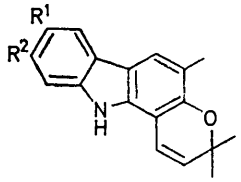


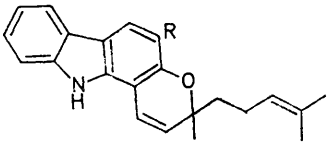
FIGURE 1 U.v. data for acridones: (a) angular chromen (9); (b) linear chromen (10); (c) citrylidene type (13)

Another set of nitrogen heterocycles containing mono- and hemi-terpenoid units has been found in the Indian plant *Murraya koenigii* Spreng. (Rutaceae), a rich source of carbazole alkaloids. These include a group of dimethylpyrano[2,3-*a*]carbazoles, *e.g.* girinimbine (20),[11d,h] koenimbine (21),[12] koenigicine (22) [12b] (otherwise koenimbidine [11e] or koenidine [13]), koenine (23),[11h,13] and koenigine (24).[13] The first two have been synthesised from the hydroxy-acetal (1) and the appropriate 3-hydroxycarbazole. Other related chromens [11e,14] and simple carbazoles [15] have been isolated.

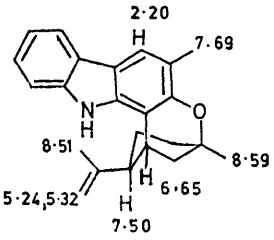
The simplest of the monoterpenoid carbazoles, mahanimbine (25), occurs naturally [11e,12a,16] in optically active form, m.p. 94—95°. Several groups have applied citral condensation to 2-hydroxy-3-methylcarbazole. (±)-Mahanimbine, m.p. 75—76°, was successfully obtained by Kureel *et al.*[17] and by Narasimhan *et al.*,[11f] the latter using pyridine containing 2% benzoic acid. Two other groups used unexpected conditions. Chakraborty and colleagues [18] report that the reaction of the carbazole with citral and pyridine proceeds at ambient temperature, while Dutta *et al.*[19] could not obtain mahanimbine by the pyridine–citral method but reported success with a Lewis-acid catalysis procedure. These last two reports however give m.p. 93—94° for (±)-mahanimbine, not depressed by admixture with the



(20) $R^1=R^2=H$
(21) $R^1=OMe, R^2=H$
(22) $R^1=R^2=OMe$
(23) $R^1=OH, R^2=H$
(24) $R^2=OMe, R^2=OH$



(25) R = Me
(26) R = H



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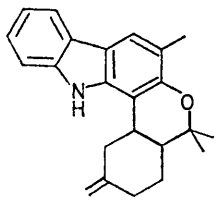

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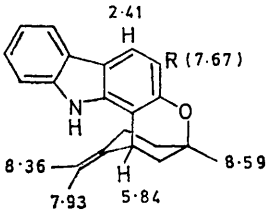
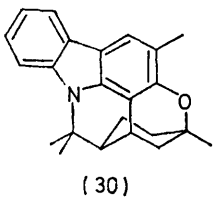


(29) R = Me
(38) R = H



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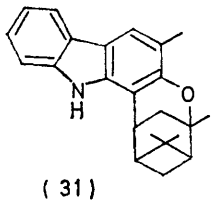


(31)

natural (+)-compound. In our hands 2-hydroxy-3-methylcarbazole (from 2-hydroxycarbazole by formylation followed by Wolff–Kishner reduction) afforded

[10] D. G. Clarke, L. Crombie, and D. A. Whiting, *J.C.S. Chem. Comm.*, 1973, 582.

[11] (*a*) D. P. Chakraborty, B. K. Barman, and P. K. Bose, *Science and Culture*, 1964, **30**, 445; (*b*) D. P. Chakraborty and B. K. Chowdhury, Proc. Vth Internat. Symp., Chemistry of Natural Products, 1968; (*c*) D. P. Chakraborty, *J. Indian Chem. Soc.*, 1969, **46**, 177; (*d*) N. L. Dutta and C. Quasim *Indian J. Chem.*, 1969, **7**, 307; (*e*) B. S. Joshi, V. N. Kamat, and D. H. Gawad, *Tetrahedron*, 1970, **26**, 1475; (*f*) N. S. Narasimhan, M. V. Paradkar, and A. M. Gokhale, *Tetrahedron Letters*, 1970, 1665; (*g*) D. P. Chakraborty and A. Islam, *J. Indian Chem. Soc.*, 1971, **48**, 91; (*h*) S. P. Kureel, R. S. Kapil, and S. P. Popli, *Chem. and Ind.*, 1970, 1262.

[12] (*a*) N. S. Narasimhan, M. V. Paradkar, and V. P. Chitguppi, *Tetrahedron Letters*, 1968, 5501; (*b*) S. P. Kureel, R. S. Kapil, and S. P. Popli, *Experientia*, 1969, **25**, 790.

[13] N. S. Narasimhan, M. V. Paradkar, and S. L. Kelkar, *Indian J. Chem.*, 1970, **8**, 473.

[14] D. P. Chakraborty and K. C. Das, *Chem. Comm.*, 1965, 967; D. P. Chakraborty, K. C. Das, and B. K. Chowdhury, *J. Org. Chem.*, 1971, **36**, 725.

[15] D. P. Chakraborty, B. K. Barman, and P. K. Bose, *Tetrahedron*, 1965, **21**, 681; D. P. Chakraborty and B. K. Chowdhury, *J. Org. Chem.*, 1968, **33**, 1265; B. K. Chowdhury and D. P. Chakraborty, *Chem. and Ind.*, 1969, 549; *Phytochemistry*, 1971, **10**, 1967.

[16] D. P. Chakraborty, K. C. Das, and P. K. Bose, *Science and Culture*, 1966, **32**, 83.

[17] S. P. Kureel, R. S. Kapil, and S. P. Popli, *Chem. Comm.*, 1969, 1120.

[18] D. P. Chakraborty, D. Chatterji, and S. N. Ganguly, *Chem. and Ind.*, 1969, 1662.

[19] N. L. Dutta, C. Quasim, and M. S. Wadia, *Indian J. Chem.*, 1969, **7**, 1168.

(±)-mahanimbine, m.p. 72—73°, after heating with citral and pyridine. Normahanimbine (26) was similarly prepared.

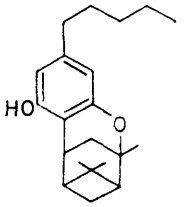
Modification of the chromen unit in mahanimbine (25) is apparent in cyclomahanimbine (27), another constituent [20] of the leaves of *M. koenigii*. We have prepared (±)-cyclomahanimbine from (±)-mahanimbine by refluxing the latter in benzene with an ion-exchange resin (Dowex-50W-X8; acid form). N.m.r. data for the synthetic compound, m.p. 140°, are shown on formula (27) and are similar to those for the natural compound. The half-height band-width [21] of the resonance at τ 7·50 (18 Hz) confirms the equatorial disposition of the isopropenyl group. Natural cyclomahanimbine is reported to have $[\alpha]_D$ 0° ($CHCl_3$), m.p. 146°.[20]

Another natural compound, curryanin, m.p. 134—137°, has been isolated from *M. koenigii* [19] and formulated as (28). Through the goodwill of Dr. Quasim we have examined a specimen and find its spectral characteristics identical with those of (27), the m.p. of a mixture being intermediate between the two values. Murryazolidine, m.p. 143°, $[\alpha]_D^{30}$ +20° ($CHCl_3$), is also assigned structure (28) in the literature,[22] but confirmation is required since a copy of the n.m.r. spectrum kindly sent to us by Dr. Chakraborty is very similar to that of our synthetic (27).

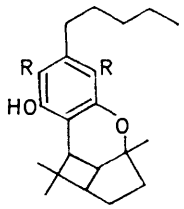
A further cyclisation product of (±)-mahanimbine was obtained on treatment with toluene-*p*-sulphonic acid at 20°. This was the isopropylidene derivative (29), characterised by the chemical shift of the benzylic proton, now further deshielded by the adjacent double bond. Related structures have been prepared in other series [1,2] and normahanimbine undergoes a similar reaction. The citrylidenecarbazole (30) has been reported in *M. koenigii* (called mahanimbidine,[20] curryangin,[23a] or murrayazoline [23b]). Although it is said to be formed by treatment of (±)-mahanimbine with toluene-*p*-sulphonic acid or certain Lewis acids [19,20,23] we have been unable to repeat the transformation: heating in pyridine also failed to give (30).

Another cyclisation pattern of the monoterpenoid chromens is exemplified in bicyclomahanimbine,[20] the structural assignment (31) being apparently influenced by an earlier,[24] incorrect structural assignment for cannabicyclol. This latter was revised by us on the basis of n.m.r. data and its manner of synthesis,[2,25] but as the revision was not accepted at the time,[26] a single crystal *X*-ray analysis was undertaken on a solvated crystal of dibromocannabicyclol.[27]

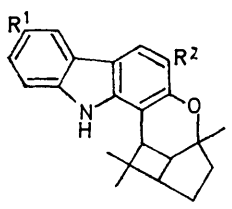
Intensity data were collected with a linear diffractometer and 2383 reflections were considered observed. The structure was solved by the heavy-atom method and refined by least-squares and difference Fourier methods. The *R*-index converged to 0·076, using anisotropic temperature factors and including hydrogen atoms, but excluding solvent of crystallisation. The solvent appeared disordered and/or a mixture of alkanes. Structure (34) is thus demonstrated for dibromocannabicyclol and cannabicyclol is represented by (33) in agreement with our original revision.[25]



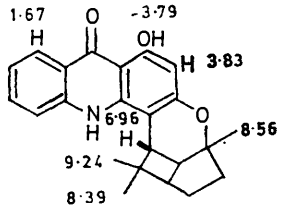
(32)



(33) R = H
(34) R = Br



(35) R^1 = H, R^2 = Me
(36) R^1 = Me, R^2 = H



(37)

General views of the molecule are given in Figure 2; numbering, detailed bond lengths and angles, are shown in Figures 3—5, respectively. Figure 6 shows the mean plane through the planar aromatic ring (χ^2 1·01) and, as expected, all atoms directly attached to this ring lie close to the plane. All atoms of the dihydropyran ring except C-14 are also near this plane. The five-membered ring adopts an envelope conformation with C-15 out of plane. The cyclobutane ring is close to planar (χ^2 2·18) and this plane forms angles of 50 and 72° with the mean planes of the aromatic ring and the cyclopentane ring. The angle between the last two planes is 79°.

From the published information,[20] and the structure of cannabicyclol (33), bicyclomahanimbine is now best represented as (35). A similar structural revision, to (36), is required for bicyclomahanimbicine described by

[20] S. P. Kureel, R. S. Kapil, and S. P. Popli, *Tetrahedron Letters*, 1969, 3857.
[21] A. Hassner and C. Heathcock, *J. Org. Chem.*, 1964, **29**, 1352.
[22] D. P. Chakraborty, A. Islam, S. P. Basak, and R. Das, *Chem. and Ind.*, 1970, 958.
[23] (*a*) N. L. Dutta, C. Quasim, and M. S. Wadia, *Indian J. Chem.*, 1969, **7**, 1061; (*b*) J. Bordner, D. P. Chakraborty, B. K. Chowdhury, S. N. Ganguli, K. C. Das, and B. Weinstein, *Experientia*, 1972, **28**, 1406.
[24] U. Claussen, F. von Spulak, and F. Körte, *Tetrahedron*, 1968, **24**, 1021; Y. Gaoni and R. Mechoulam, *Fortschr. Chem. Org. Naturstoffe*, 1967, **25**, 175.
[25] L. Crombie and R. Ponsford, *Chem. Comm.*, 1968, 894; L. Crombie, R. Ponsford, A. Shani, B. Yagnitinsky, and R. Mechoulam, *Tetrahedron Letters*, 1968, 5771.
[26] V. V. Kane and R. K. Razdan, *J. Amer. Chem. Soc.*, 1968, **90**, 6551; *Tetrahedron Letters*, 1969, 591.
[27] Preliminary communication, M. J. Begley, D. G. Clarke, L. Crombie, and D. A. Whiting, *Chem. Comm.*, 1970, 1547.

Kureel *et al.*[28] In the acridone series discussed above, an analogous cyclol compound (37) can be obtained photochemically from the chromen (9), and on treatment with boron trifluoride–ether complex in benzene. It is also formed in small quantity from 1,3-dihydroxyacridone on heating with citral and pyridine.

One of the cyclobutyl methyl groups in cannabicyclol (33) resonates at τ 9·22; other cyclol types, *e.g.* (35)—(37), show a similar high-field methyl resonance. Such high-field methyl groups attached to cyclobutane rings have been recorded [29] but in the present case molecular models of (33) suggest a contribution from aryl shielding of one methyl group. The *X*-ray data enable more reliable estimates to be made. The methyl hydrogen atom closest to the aryl ring is 3·36 Å from the centre of the ring, and 2·44 Å from the mean plane of the ring. Estimations by Johnson and Bovey's method [30] show that the positive shielding expected is in fact small (+0·1 to +0·2 p.p.m.). The *X*-ray study reveals C-20 in close proximity to the *endo*-protons of C-15 and C-16 in the five-membered ring [the bond angles show the methyl group to be distorted away from the methylenes: $\angle$C(7)C(18)C(20) = $\angle$C(12)C(18)C(20) = 117°].

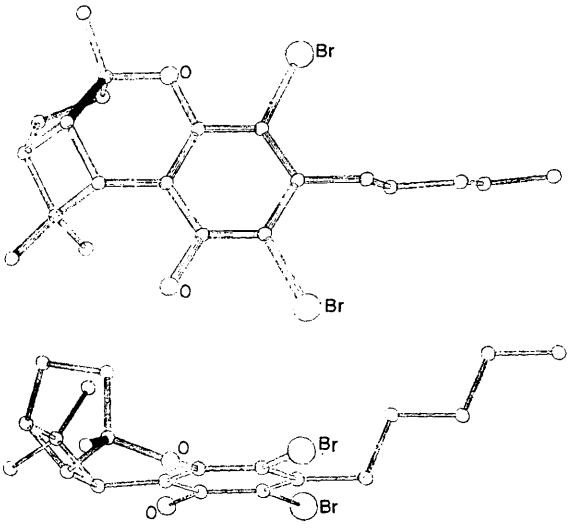


FIGURE 2 General views of the dibromocannabicyclol molecule

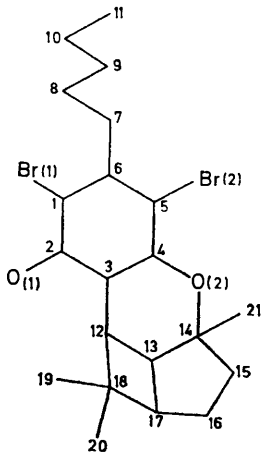


FIGURE 3 Numbering of the dibromocannabicyclol molecule

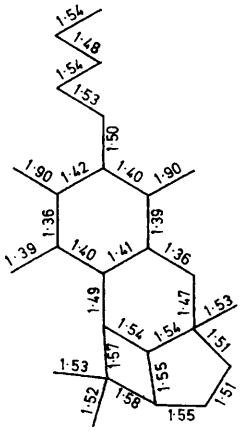
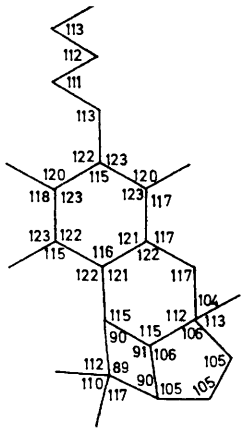


FIGURE 4 Bond lengths (Å); mean standard deviations 0·01 Å



O(2) — 14 — 15	111
13 — 14 — 21	112
12 — 18 — 20	117
17 — 18 — 19	111

FIGURE 5 Bond angles (°); mean standard deviations 1°

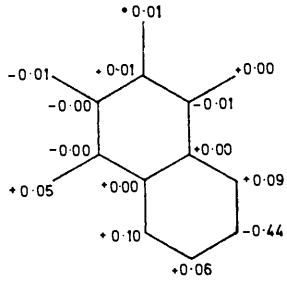


FIGURE 6 Deviations (Å) from the mean plane through the aromatic ring

[28] S. P. Kureel, R. S. Kapil, and S. P. Popli, *Chem. and Ind.*, 1970, 958.

[29] G. Zweifel and M. C. Brown, *J. Amer. Chem. Soc.*, 1964, **86**, 393.

[30] C. E. Johnson, jun., and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

EXPERIMENTAL

Satisfactory analytical and spectroscopic data were obtained for all compounds described in this section; these data are listed in Supplementary Publication No. SUP 20916 (21 pp.).* N.m.r. data quoted in the Discussion section were obtained for solutions in deuteriochloroform. T.l.c. silica gel G layers (0·3 mm) were used; in preparative work (p.l.c.) layers of silica gel B or HF254 were employed. Organic solutions were dried over magnesium sulphate and evaporated at reduced pressure.

1,3-*Dihydroxyacridone*.—Anthranilic acid (68·5 g, 0·5 mol), phloroglucinol (63 g, 0·5 mol), and zinc chloride (freshly fused; 67·5 g, 0·5 mol) were heated together in n-butanol, with continuous removal of water. After 6 h the orange precipitate was collected and stirred at 65° for 2 h in aqueous 2% sodium hydroxide (2 dm³). The cooled solution was filtered and acidified. The precipitate was filtered off, washed, and dried by azeotropic distillation with benzene, to yield 1,3-dihydroxyacridone (54 g, 40%). This was refluxed with acetic anhydride (300 cm³) and dry sodium acetate (40 g) for 2 h. The cooled solution was poured onto ice and set aside overnight. The precipitate was collected and recrystallised to provide 1,3-diacetoxyacridone (8), m.p. 205—206° (lit.,[9] 205—207°) (30 g, 40%). The whole product in methanol (300 cm³) was refluxed with potassium carbonate (30 g) for 1·5 h. The concentrated solution was acidified. The yellow precipitate was filtered off, washed, and recrystallised from acetone–ethyl acetate to yield 1,3-dihydroxyacridone (5 g, 22%).

De-N-methylnoracronycine (5).—1,3-Dihydroxyacridone (4·54 g, 0·02 mol) was heated to 150° in dry pyridine (7·02 g, 0·08 mol). 3-Hydroxyisovaleraldehyde dimethyl acetal (5·92 g, 0·04 mol) was added dropwise over 30 min. Two more portions of the acetal (5·92 g each) were added after 4 and 8 h, and refluxing was continued for 8 h more (20 h total). The mixture was evaporated and the residue chromatographed on a silica gel column. After washing with benzene–chloroform (1 : 1) elution was continued with chloroform–ethyl acetate (9 : 1). Evaporation of the eluate gave a mixture (1·86 g, 32%), m.p. 226—234°, of the chromens (4) and (5). Repeated crystallisation from benzene–ethyl acetate afforded de-*N*-methylnoracronycine (5), m.p. 247° (lit.,[5g] 247°), identical (mixed m.p. and spectroscopic criteria) with the natural compound.

Acronycine (2).—De-*N*-methylnoracronycine (0·1 g) was refluxed in acetone (15 cm³) with methyl iodide (4 cm³) over dry potassium carbonate (4 g) for 48 h. After filtration, the solution was evaporated, and the residue was crystallised from aqueous methanol to afford acronycine (86 mg), m.p. 175—176° (lit.,[5] 175—176°), identical (mixed m.p. and spectra) with the natural compound.

Acronycine (2) *and Isoacronycine* (6).—The mixture (0·75 g) of 2,2-dimethylchromens from 1,3-dihydroxyacridone was refluxed in acetone (150 cm³) with methyl iodide (5 cm³) over potassium carbonate for 12 h. Two more portions of methyl iodide (5 cm³) were added at 12 h intervals. The total reflux time was 48 h. The solution was filtered and evaporated. The residue was extracted with ethyl acetate and the solution concentrated and applied to 20 × 20 cm Kieselgel G (1 mm) plates. Elution with benzene–ethyl acetate (12 : 1) gave two bands; that of lower R_F gave, on extraction, acronycine, m.p. 175—176° (0·6 g), identical with the above sample. The band of higher R_F afforded isoacronycine (0·21 g), m.p. 159° (from aqueous methanol). The compound has subsequently been reported.[31]

Condensation of 1,3-*Dihydroxyacridone with Citral*.—(*a*) 1,3-*Dihydroxyacridone* (2·27 g, 0·01 mol; purified by crystallisation of the acetate) was heated at 120° in pyridine (10 g). Citral (1·52 g, 0·01 mol) was added dropwise (30 min), and refluxing was continued with stirring for 7 h. More citral (1·52 g) was added and refluxing was continued for 14 h. The mixture was evaporated and the residue separated by p.l.c. [light petroleum–ether (1 : 1)]. Four bands were removed. The material from the slowest-moving band was repurified by p.l.c. with the same solvent, and then crystallised from ethanol to yield 3,12-*dihydro*-6-*hydroxy*-3-*methyl*-3-(4-*methylpent*-3-*enyl*)*pyrano*[2,3-c]-*acridin*-7-*one* (9) (1·25 g, 38%), m.p. 199—200°. The next band was eluted, repurified by p.l.c., and crystallised from ethanol to give 2,11-*dihydro*-5-*hydroxy*-2-*methyl*-2-(3-*methylbut*-2-*enyl*)*pyrano*[3,2-b]*acridin*-6-*one* (10) (620 mg, 19%), m.p. 238—240°. The third most polar compound was also rechromatographed and yielded the *citrylideneacridone* (13) (200 mg, 6%), m.p. 232° (from benzene). The least polar (highest R_F) band was extracted and the extracts were repurified by p.l.c. to afford the *isopropenylacridone* (14) (200 mg, 6%).

(*b*) A similar reaction was carried out at 160° for 18 h. The mixture was evaporated and the residue refluxed with acetone (30 cm³) for 4 h. The yellow precipitate was filtered off, and the filtrate was evaporated and chromatographed. The precipitate yielded the citrylideneacridone (13) (10%) and the isopropenyl compound (14) (3%); the filtrate afforded the chromens (9) (29%) and (10) (6%), together with the *cyclol* (37) (100 mg, 3%), m.p. 198—200° (from ethanol). This product formed a crystalline *boron trifluoride complex*, m.p. 270—275°, which decomposed slowly on boiling in methanol.

Preparation of the Cyclol (37).—(*a*) The chromen (9) (300 mg) in acetone (90 cm³) and t-butyl alcohol (90 cm³) was irradiated with a 450 W medium-pressure mercury lamp for 16 h. The solution was evaporated and the residue crystallised from acetone–light petroleum (b.p. 80—100°) to yield the cyclol, m.p. 198—200° (180 mg, 60%).

Methylation of the Chromens (9) *and* (10).—The angular chromen (9) (100 mg) was refluxed with methyl iodide (1 cm³) in acetone (3 cm³) over dry potassium carbonate (200 mg) for 24 h. More methyl iodide (1 cm³) was added and refluxing was continued for 24 h more. The solution was filtered and evaporated. The residue was chromatographed [light petroleum–ether (1 : 1)]. The major (yellow) band was extracted, and provided the N-*methyl derivative* (11), m.p. 123—124° (from ethanol) (47 mg, 45%), giving a blue-green colour with iron(III) chloride. A similar reaction was effected with the linear chromen (10) (26 mg) and methyl iodide (2 cm³) in acetone (3 cm³) over potassium carbonate (150 mg). Isolation of the major product in the same manner gave the N-*methyl derivative* (12) (26 mg, 96%), m.p. 103—105°.

Gibbs' Reaction.—A borate buffer, pH 9·2, was prepared from aqueous boric acid (50 cm³; 0·2M), potassium chloride (50 cm³; 0·2M), and sodium hydroxide (26·7 cm³; 0·2M), made up to 200 cm³ with water. The phenol (*ca.* 2 mg) in dry pyridine (1 cm³) was mixed with 2,6-dichloro-*p*-benzoquinone 4-chloroimide (5 cm³ of 0·2% solution in pyridine;

* For details of Supplementary Publications see Notice to Authors No. 7 (*J.C.S. Perkin I*, 1972, Index Issue).

[31] C. S. Oh and C. V. Greco, *J. Heterocyclic Chem.*, 1970, **7**, 261.

freshly prepared) and diluted to 125 cm³ with buffer. The spectrum (500—700 nm) was recorded at 10 min intervals.

The chromen (10) developed $\lambda_{max.}$ 669 nm (ε 8350) after 120 min; the chromen (18) developed $\lambda_{max.}$ 671 nm (ε 25,000) after 120 min. The chromens (9) and (17) developed no comparable maxima during this period.

Conversion of the Chromen (9) *into the Citrylideneacridone* (13). The chromen (9) (100 mg) was heated in pyridine (5 cm³) under nitrogen for 24 h at 160—170°. No reaction was indicated by t.l.c., and the temperature was raised to 190° and maintained for 24 h. Pyridine was evaporated off and the residue was purified by p.l.c. The citrylideneacridone (13) (30 mg), m.p. 231° (from benzene), was isolated, and identified by comparison with the foregoing sample.

Isomerisation of the Citrylideneacridone (13).—The citrylidene compound (13) (100 mg) was refluxed for 8 h in benzene (2 cm³) with toluene-*p*-sulphonic acid (50 mg). The product was evaporated and separated by p.l.c.; one new compound was obtained, shown to be the isopropenylacridone (14), m.p. 230°, by comparison with the authentic sample.

Cyclisation of the Chromen (9).—The chromen (9) (100 mg) was heated under reflux in dry benzene (3 cm³) with toluene-*p*-sulphonic acid. The product was isolated as the previous experiment, and proved to be the *isopropenylacridone* (14), m.p. 230° (from benzene) (45 mg).

Acetylation of the Citrylideneacridone (13).—The acridone (13) was refluxed in an excess of pyridine and acetic anhydride (1 : 3). The product was acidified, and extracted with ethyl acetate. P.l.c. of the concentrated extract (light petroleum–ether) afforded the *acetyl derivative*, m.p. 240—241° (from benzene).

Dibromocannabicyclol.—A solution (2 cm³) of bromine in dioxan (76·5 mg cm^{-3}) was added to cannabicyclol (100 mg) in dioxan (2 cm³) containing dry sodium carbonate (83 mg). The solution was filtered after 25 min, concentrated, and the product was purified by p.l.c. The major band afforded a gum which crystallised slowly at 0°. Several recrystallisations from light petroleum, at −20°, gave *dibromocannabicyclol*, m.p. 73—74° (127 mg, 84%).

Condensation of 1,3-*Dihydroxyacridone with Farnesal.*—1,3-Dihydroxyacridone (2·27 g, 0·01 mol) was heated to 150° in pyridine (7·9 g, 0·1 mol). Farnesal (2·2 g, 0·01 mol) was added dropwise over 30 min, and the reaction was continued for 24 h with stirring. More farnesal (2·2 g) was added after 4 h. The mixture was evaporated and the residue applied to p.l.c. plates. Elution with light petroleum (b.p. 60—80°)–ether (1 : 1) gave five yellow bands. That of lowest R_F gave the *angular chromen* (17), yellow needles from ethanol, m.p. 174—175° (1·53 g, 35%). The *linear chromen* (18) from the next band, formed yellow plates, m.p. 229—230° (88 mg, 2%). The third band provided the *citrylidene compound* (19), yellow needles from ethanol, m.p. 168·5—169·5° (110 mg, 2·5%). The two bands of higher R_F gave all-*trans*-farnesal and *cis*-2,*trans*-6-farnesal, identified by their n.m.r. data.

2-*Hydroxy*-3-*methylcarbazole.*—2-Hydroxycarbazole (50 g) in dry ether (700 cm³) with zinc cyanide (50 g) and aluminium chloride (1 g) was cooled in ice, and saturated with dry hydrogen chloride gas during 2·5 h. The mixture was set aside overnight; then the solvent was decanted, and the residue boiled with water (500 cm³) for 30 min. The product was extracted with ethyl acetate (5 × 300 cm³) and the extracts were washed, dried, and evaporated. The residue was chromatographed on silica gel (Grace; 100—200 mesh). The light petroleum eluate was discarded. Elution with benzene–light petroleum (1 : 1) gave 2-hydroxycarbazole-3-carbaldehyde, m.p. 236—237° (lit.,[32] 240°) (14·4 g). The aldehyde (11·2 g) in diethylene glycol (150 cm³) was treated with potassium hydroxide (11 g) and hydrazine hydrate (20 cm³). After refluxing for 2 h, the mixture was distilled until the liquid temperature reached 200°. The reaction was continued at 200° for 3 h. The cooled mixture was neutralised and extracted with ethyl acetate. The dried extracts were evaporated and the residue chromatographed on silica gel with gradient elution (0—50% chloroform in benzene); fractions were monitored by t.l.c. The major product was isolated by evaporation and purified by sublimation to provide 2-hydroxy-3-methylcarbazole (3·5 g).

(±)-*Mahanimbine* (25).—2-Hydroxy-3-methylcarbazole (500 mg, 0·003 mol) was heated to 110° in pyridine (900 mg, 0·004 mol) under nitrogen. Citral (440 mg, 0·003 mol) was added dropwise during 30 min, and the reaction was continued with stirring for 24 h; the product was then evaporated. P.l.c. [benzene–light petroleum (b.p. 60—80°) (2 : 1)] showed one fluorescent band which on extraction supplied (±)-mahanimbine (25), m.p. 72—73° (100 mg). This product was not distinguishable (u.v., i.r., n.m.r., and mass spectrometry) from a specimen of (+)-mahanimbine isolated [11] by us from dried leaves of *Murraya koenigii* Spreng.

Cyclisation of (±)-*Mahanimbine.*—(*a*) (±)-Mahanimbine (100 mg) in dry benzene (15 cm³) was refluxed over Dowex-50W-X8 (H^+) resin (3 g) for 6 days. Filtration and evaporation gave a brown residue, which was separated by p.l.c. Two bands were extracted; that of higher R_F yielded unchanged (±)-mahanimbine; the other provided the *isopropenylcarbazole* (27), m.p. 140° (16 mg).

(*b*) (±)-Mahanimbine (51 mg) was stirred at room temperature for 3 h in dry benzene (30 cm³) with toluene-*p*-sulphonic acid (50 mg). The black solution was filtered and evaporated. The dark residual gum was separated by p.l.c. [benzene–light petroleum (b.p. 40—60°) (1 : 1)]. One colourless non-crystalline product (5 mg) was isolated, which proved to be the *isopropylidenecarbazole* (29).

Normahanimbine.—2-Hydroxycarbazole (53 g, 0·29 mol) in pyridine (104 g, 1·33 mol) was heated at 110° under nitrogen. Citral (51 g, 0·335 mol) was added dropwise during 30 min and the reaction was continued for 6 days. The mixture was evaporated and the residue chromatographed on a silica gel column. Elution with benzene–light petroleum (b.p. 60—80°) (3 : 1) gave only one compound, *normahanimbine* (26), m.p. 63—65° (from n-pentane) (16 g, 17%).

Cyclisation of Normahanimbine.—Normahanimbine (1 g) was heated with toluene-*p*-sulphonic acid (100 mg) in dry benzene (25 cm³) for 4 h, under nitrogen. The mixture was poured into water and the organic layer separated. The aqueous layer was extracted with ethyl acetate. The organic extracts were dried and evaporated. The residue was chromatographed on plates [benzene–light petroleum [b.p. 60—80° (1 : 1)]. The *isopropylidenecarbazole* (38) was the only product isolated (5%). It failed to crystallise.

Crystal Structure Determination of Dibromocannabicyclol.—Dibromocannabicyclol was crystallised at −20° from light petroleum (b.p. 40—60°) as a *ca.* 2 : 1 solvate. Oscillation

[32] M. R. R. Bhagwanth, A. V. Rama Rao, and K. Venkataraman, *Indian J. Chem.*, 1969, **7**, 1065.

and Weissenberg photographs were taken about all three crystallographic axes to determine the unit cell parameters. For intensity measurement, a crystal, *ca.* 0·75 × 0·45 × 0·20 mm, was mounted (in a sealed capillary tube to prevent decomposition) about the *b* axis on a Hilger and Watts linear diffractometer. With Mo-K_α radiation, intensity data were collected on the levels $h0$—$10l$ by the moving-crystal stationary-counter scan method. Each reflection was measured twice, and the mean taken in data reduction. Reflections with a mean net count less than 3 standard deviations were considered unobserved, leaving 2383 observed reflections which were used in the subsequent refinement. No absorption corrections were made. Data reduction and subsequent crystallographic calculations were performed using the National Research Council (Ottawa) programs of Ahmed, Hall, Pippy, and Saunders. Atomic scattering factors were taken from standard tables.[33]

Crystal Data.—$C_{21}H_{28}Br_2O_2$, M = 472·3. Triclinic, a = 9·14(3), b = 10·20(3), c = 15·51(4) Å, α = 112·9(4), β = 87·2(6), γ = 116·0(4)°, U = 1183 Å^3, Z = 2, D_c = 1·40 (assuming 2 : 1 $C_{21}H_{28}Br_2O_2 : C_6H_{14}$), $F(000)$ = 480. Space group $P\bar{1}$ assumed and verified by subsequent refinement. Mo-K_α radiation, λ = 0·7107, μ(Mo-K_α) = 36·5 cm^{-1}.

The co-ordinates of the two independent bromine atoms were found from a Patterson synthesis using the observed intensity data, sharpened by $1/Lp$ corrections. A three-dimensional Fourier summation phased on the bromine atoms, revealed the remaining 23 non-hydrogen atoms.

Initially five cycles of block-diagonal least-squares refinement of atomic positions and isotropic temperature factors were carried out with all the data and unit weights. A weighting scheme was then adopted of the form $w = 1/\{1 + [|F_o| - p_2/p_1]^2\}$ with p_1 = 15·0 and p_2 = 12·0, and the temperature factors of the bromine atoms were allowed to vary anisotropically. Two further cycles reduced the value of R to 0·096. A difference synthesis was then calculated and this revealed the location of the petroleum molecule. This appeared as a column of electron density through the centre at ($\frac{1}{2}1\frac{1}{2}$) running in the direction towards ($0\frac{1}{2}\frac{1}{2}$). The positions of three carbon atoms were chosen within this column so that, together with their centrosymmetrically related positions, they might represent a molecule of n-hexane. A further five cycles of refinement were then calculated in which the temperature factors of the remaining atoms in the cannabicyclol molecule were allowed to vary anisotropically and the three carbon atoms of the petroleum molecule were included with isotropic temperature factors. The value of R was thus reduced to 0·073. The difference synthesis was further examined and found to reveal the approximate positions of all the hydrogen atoms. The positions of the hydrogen atoms were calculated accurately from bond length and angle considerations and these were included in the structure factor calculations. Three final rounds of least squares refinement, including but not refining the hydrogen atoms, reduced R to 0·064 after a total of 15 cycles, the largest parameter shifts being then of the order of 0·3σ. An examination of the bond lengths and angles of the refined atoms in the hexane molecule showed that these did not make chemical sense. These atoms were therefore eliminated from the structure factor calculation which, without them, showed an agreement factor of 0·076. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20916 (21 pp.) (see footnote on p. 1004). A final difference map was calculated which showed the same column of electron density of the petroleum molecule. There were no distinct peaks for the individual atoms, which must be highly disordered; probably a mixture of pentane and hexane randomly occupy this space in the crystal structure. The accuracy of the cannabicyclol structure was confirmed from the final difference map which showed no peaks or depressions >0·3 eÅ^{-3} apart from the position of the petroleum molecule.

TABLE 1

Atomic co-ordinates with standard deviations in parentheses

Atom	x/a	y/b	z/c
Br(1)	−0·3185(1)	0·7862(1)	0·2223(1)
Br(2)	0·3590(1)	0·9157(1)	0·2153(1)
O(1)	−0·3247(7)	0·6270(8)	0·0101(4)
O(2)	0·2401(6)	0·7380(7)	0·0134(4)
C(1)	−0·1390(10)	0·7755(9)	0·1580(6)
C(2)	−0·1690(9)	0·7002(9)	0·0617(6)
C(3)	−0·0457(9)	0·6851(9)	0·0071(5)
C(4)	0·1126(9)	0·7529(9)	0·0572(6)
C(5)	0·1414(9)	0·8296(9)	0·1552(5)
C(6)	0·0183(10)	0·8435(10)	0·2102(6)
C(7)	0·0508(12)	0·9259(11)	0·3164(6)
C(8)	0·1165(13)	1·1071(11)	0·3530(6)
C(9)	0·1580(15)	1·1880(13)	0·4617(7)
C(10)	0·2367(20)	1·3650(15)	0·4981(9)
C(11)	0·2851(24)	1·4490(18)	0·6062(9)
C(12)	−0·0805(9)	0·5936(9)	−0·0974(6)
C(13)	0·0706(10)	0·5922(9)	−0·1459(5)
C(14)	0·2381(9)	0·7207(10)	−0·0851(6)
C(15)	0·2645(9)	0·8740(9)	−0·0905(6)
C(16)	0·1868(11)	0·8218(11)	−0·1898(7)
C(17)	0·0345(10)	0·6585(10)	−0·2122(6)
C(18)	−0·1221(10)	0·6579(10)	−0·1650(6)
C(19)	−0·2802(11)	0·5327(12)	−0·2340(7)
C(20)	−0·1284(12)	0·8166(11)	−0·1185(6)
C(21)	0·3776(11)	0·6769(11)	−0·1182(7)
H(7a)	0·1411	0·9013	0·3418
H(7b)	−0·0622	0·8768	0·3438
H(8a)	0·2270	1·1560	0·3225
H(8b)	0·0246	1·1326	0·3311
H(9a)	0·2422	1·1533	0·4827
H(9b)	0·0457	1·1457	0·4911
H(10a)	0·3447	1·4071	0·4651
H(10b)	0·1491	1·4003	0·4786
H(11a)	0·3714	1·4154	0·6258
H(11b)	0·1759	1·4086	0·6393
H(11c)	0·3405	1·5774	0·6327
H(12)	−0·1608	0·4713	−0·1070
H(13)	0·0684	0·4765	−0·1861
H(15a)	0·3948	0·9566	−0·0782
H(15b)	0·2048	0·9333	−0·0378
H(16a)	0·2726	0·8088	−0·2394
H(17)	0·0176	0·5876	−0·2879
H(19a)	−0·2932	0·5671	−0·2906
H(19b)	−0·2755	0·4201	−0·2593
H(19c)	−0·3911	0·5193	−0·2022
H(20a)	−0·0378	0·8889	−0·0544
H(20b)	−0·2495	0·7978	−0·0978
H(20c)	−0·1048	0·8768	−0·1649
H(21a)	0·3430	0·5546	−0·1293
H(21b)	0·4823	0·7589	−0·0641
H(21c)	0·4066	0·6885	−0·1848
H[O(1)]	−0·3944	0·6466	0·0583

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[33] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2

Thermal parameters

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Br(1)	0·0149(1)	0·0197(2)	0·0079(1)	0·0115(2)	0·0111(2)	0·0159(3)
Br(2)	0·0129(1)	0·0266(2)	0·0061(1)	0·0093(2)	−0·0007(1)	0·0158(3)
O(1)	0·0090(9)	0·0210(12)	0·0064(4)	0·0081(11)	0·0004(9)	0·0099(16)
O(2)	0·0108(8)	0·0170(10)	0·0048(3)	0·0064(9)	0·0035(8)	0·0130(15)
C(1)	0·0125(13)	0·0132(13)	0·0055(5)	0·0092(13)	0·0066(12)	0·0118(21)
C(2)	0·0095(12)	0·0133(13)	0·0061(5)	0·0108(13)	0·0048(12)	0·0070(20)
C(3)	0·0100(11)	0·0119(12)	0·0041(4)	0·0068(12)	0·0038(11)	0·0059(19)
C(4)	0·0105(12)	0·0131(13)	0·0051(5)	0·0083(13)	0·0024(11)	0·0091(21)
C(5)	0·0096(11)	0·0156(13)	0·0048(4)	0·0107(13)	0·0020(11)	0·0091(20)
C(6)	0·0142(13)	0·0130(12)	0·0053(5)	0·0089(13)	0·0037(12)	0·0115(21)
C(7)	0·0172(16)	0·0170(15)	0·0055(5)	0·0108(15)	0·0064(14)	0·0131(26)
C(8)	0·0209(19)	0·0160(16)	0·0048(5)	0·0061(14)	0·0018(15)	0·0090(28)
C(9)	0·0279(25)	0·0215(20)	0·0061(6)	0·0093(18)	0·0048(19)	0·0227(37)
C(10)	0·0419(39)	0·0211(23)	0·0070(8)	0·0021(21)	−0·0007(21)	0·0174(48)
C(11)	0·0539(50)	0·0277(29)	0·0065(8)	0·0034(24)	0·0041(31)	0·0273(62)
C(12)	0·0106(12)	0·0112(12)	0·0055(5)	0·0074(13)	0·0023(12)	0·0054(20)
C(13)	0·0128(13)	0·0109(12)	0·0042(4)	0·0036(11)	0·0015(11)	0·0074(20)
C(14)	0·0102(12)	0·0134(13)	0·0053(5)	0·0057(13)	0·0038(12)	0·0086(21)
C(15)	0·0094(12)	0·0116(12)	0·0055(5)	0·0056(13)	0·0018(12)	0·0030(20)
C(16)	0·0160(16)	0·0150(15)	0·0063(6)	0·0113(15)	0·0039(14)	0·0071(25)
C(17)	0·0134(13)	0·0139(14)	0·0045(4)	0·0052(13)	0·0030(12)	0·0082(23)
C(18)	0·0119(13)	0·0133(13)	0·0051(5)	0·0054(13)	−0·0000(12)	0·0064(21)
C(19)	0·0143(15)	0·0206(18)	0·0054(5)	0·0080(16)	−0·0005(14)	0·0076(27)
C(20)	0·0189(17)	0·0174(16)	0·0058(5)	0·0092(15)	0·0036(15)	0·0194(28)
C(21)	0·0129(14)	0·0196(17)	0·0061(5)	0·0044(15)	0·0054(14)	0·0173(26)

In the form: $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{13})$; figures in parentheses indicate the standard deviations ($\times 10^{-4}$)

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