Unsaturated Steroids. Part 13.[1] Further Observations upon the Formation of Aromatic Ring C Steroids: *X*-Ray Structure of 22,23-Dibromo-10-methyl-19-noranthraergosta-5,7,9(10),14-tetraene and of 2β,3α,22,23-Tetrabromo-18-nor-17-isoergosta-8(9),11,13(14)-triene.

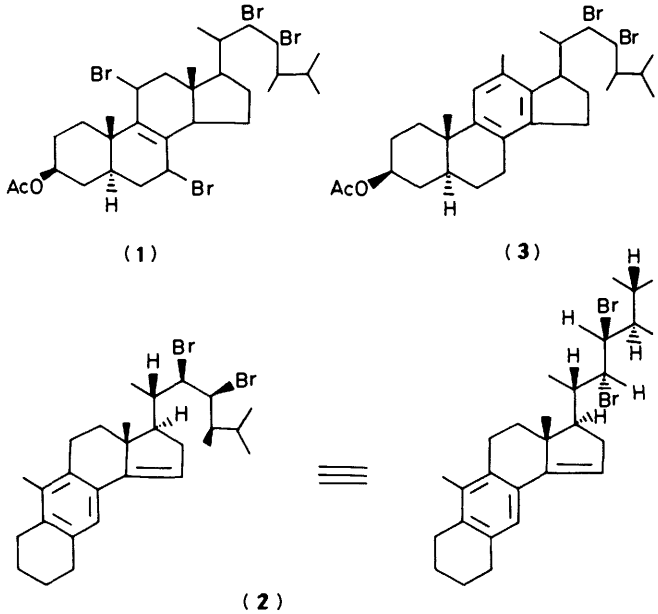
George Ferguson,* Branko Kaitner, and Arpad F. Somogyvari
Department of Chemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1
Victor I. Bendall, W. Basil Whalley,* Clive L. Yeates, (in part) Richard Edmunds, and John M. Midgley
The School of Pharmacy, University of London, 29–39 Brunswick Square, London WC1N 1AX

The aromatisation of ring C in 7α,11α,22α,23α-tetrabromo-5α-ergost-8-en-3β-yl acetate (**1**), with the concomitant elimination of C-18 as methyl halide, has been investigated. The structures and absolute stereochemistry of the two steroids named in the title, and produced in the aromatisation have been defined by *X*-ray crystallography: the mechanisms of these aromatisations are discussed. Crystals of the anthrasteroid (**2**) are monoclinic, space group *F*2 with eight molecules in a cell of dimensions a = 31.38(2), b = 5.918(2), c = 28.469(9) Å, β = 102.20(1)°. Crystals of the 18-nor-17-isoergosta-8,(9),11,13(14)-triene derivative (**4**) are monoclinic, space group $P2_1$, with two molecules in a cell of cell dimensions a = 10.512(2), b = 7.682(1), c = 17.148(2) Å, β = 91.59(2)°. Both structures were solved by the heavy atom method and refined by full-matrix least-squares calculations. For (**2**), R = 0.051, R_w = 0.055 for 853 observed reflections; the corresponding values for (**4**) are 0.052, 0.055 and 1 136 respectively. In (**2**), rings A and C adopt symmetrical half-chair conformations (but ring A is disordered over two sites); the aromatic ring B is essentially planar and the cyclopentene ring D has a C-17 envelope conformation. Molecule (**4**) has ring A in a distorted chair conformation with *trans* di-axial bromine atoms, ring B is in a sofa conformation, aromatic ring C is planar, and ring D is a C-16 envelope. The bromine-containing side chain is maximally extended in both (**2**) and (**4**).

During previous investigations[2] concerning the acid-catalysed aromatisation of ring C in 7α,11α,22α,23α-tetrabromo-5α-ergost-8-en-3β-yl acetate (**1**) we have observed that (**1**) decomposes at room temperature in the presence of a trace of acid to eliminate a molar proportion (approximately) of methyl bromide, the identity of which was established on the basis of its n.m.r. and mass spectra and its retention time on g.l.c. We have extensively investigated this observation in an attempt to exploit its synthetic possibilities since theoretical considerations indicate that the C-methyl group eliminated should be C-18. Although our results confirm this prediction, success has been limited by (*a*) inversion[2] of configuration at C-17 during the reaction, (*b*) the great difficulty of separating the reaction products, even with h.p.l.c., and (*c*) the resistance of most of the products to crystallisation.

Thus, when the tetrabromide (**1**) was dissolved in chloroform, methyl bromide was slowly evolved together with hydrogen bromide. Extensive investigations (including a wide variety of solvents) into this reaction were carried out in attempts to isolate and characterise the steroidal products, the majority of which apparently arise by elimination of the C-18 methyl residue and the consequent aromatisation of ring C.

The first crystalline product obtained was an aromatised steroid, which on the basis of the n.m.r. spectrum was tentatively formulated as the anthra steroid (**2**); this was confirmed by *X*-ray crystallography as shown in Figure 1 which also shows the absolute configuration as determined by anomalous dispersion measurements. Details of molecular geometry are summarised in Table 1. The bond lengths and angles are in accord with accepted values; ring A has a half-chair conformation with disordered atoms C(2) and C(3) alternately above and below the plane through atoms C(4), C(5), C(6), and C(1). Aromatic ring B is close to planar; ring C has a half-chair conformation with C(12) and C(13) respectively above (0.43) and below (−0.33 Å) the plane through atoms C(14), C(8), C(9), and



C(11). The cyclopentene ring D is in an envelope conformation with C(17) at the flap and 0.55 Å from the plane of C(13)–C(16). The bromine-containing side chain extends equatorially from C(17) and is maximally extended (torsion angles close to 180°) with the bromine atoms fully staggered. In the crystal structure (Figure 2) the molecules are separated by normal van der Waals distances; there are no unusual intermolecular contacts.

The genesis of the saturated ring A, in (**2**) is presumably from the 3α-acetoxyanthra steroid yielding a 2,3-ene which either during the aromatisation process and/or during the isolation, is reduced (by HBr?) to (**2**).

In further attempts to isolate crystalline products from the partially purified mixture of aromatised products, the 3β-acetoxy group of the mixture was replaced by bromine, using triphenylphosphine dibromide. The applicability of this approach was initially established by the conversion (in moderate yield) of 22,23-dibromo-12-methyl-18-nor-5α-ergosta-8(9),11,13(14)-triene-3β-ol (**3**)[2] into the corresponding crystalline 3α-bromo derivative. Using this method, three crystalline products were obtained from the mixture derived from the aromatisation of (**1**). The major product, the structure and absolute stereochemistry of which were established by *X*-ray crystallography, was 2β,3α,22α,23α-tetrabromo-18-nor-5α-17-isoergosta-8(9),11,13(14)-triene (**4**): also see Figure 1. Table 1

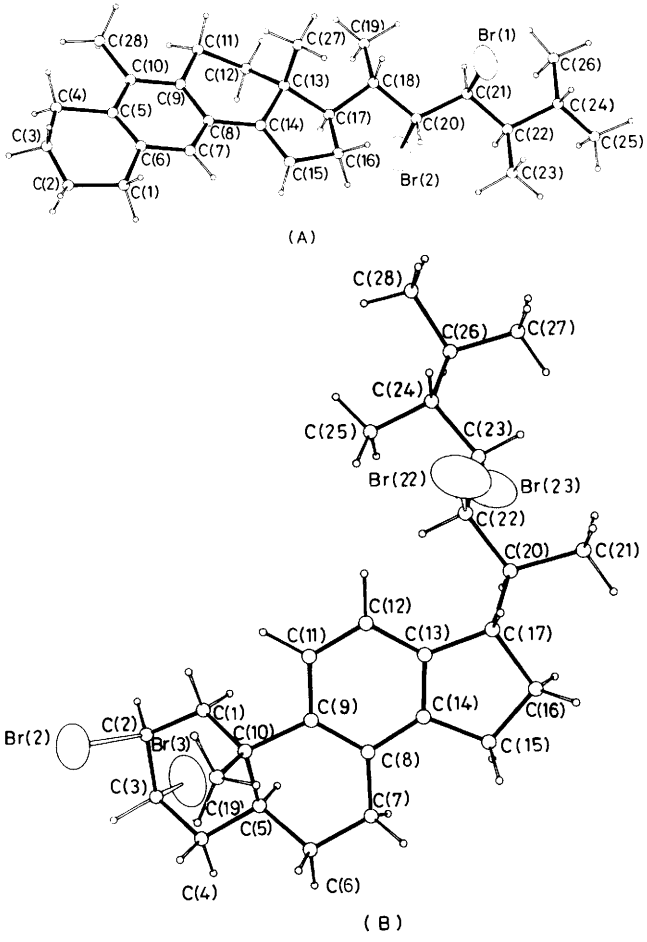
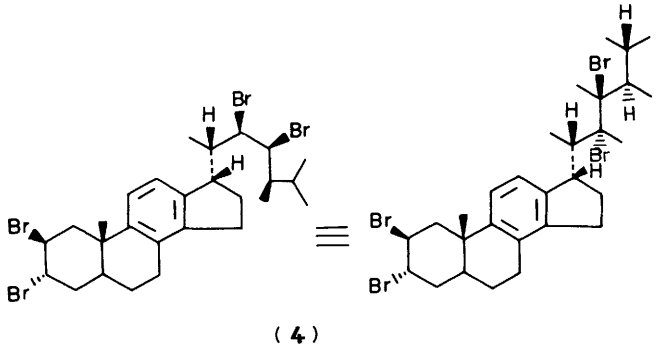


Figure 1. Views of $C_{28}H_{40}Br_2$ (**2**) (A) and of $C_{27}H_{38}Br_4$ (**4**) (B), showing the crystallographic numbering schemes and absolute stereochemistries. For clarity, the carbon and hydrogen atoms are shown as spheres of arbitrary size. Only one of the two observed conformations of the C(2)–C(3) moiety in (**2**) is shown.



(**4**)

Table 1. Summary of mean bond lengths for (**2**) and (**4**)

	(**2**)	(**4**)
$C(sp^3)$–Br	1.98(2)	1.98(2)
$C(sp^3)$–$C(sp^3)$	1.53(3)	1.54(3)
$C(sp^3)$–$C(sp^2)$	1.51(3)	1.51(3)
Aromatic $C(sp^2)$–$C(sp^2)$	1.40(3)	1.39(3)
$C(sp^2)$–$C(sp^2)$	1.49(2)	
$C(sp^2)$–$C(sp^2)$	1.28(2)	

contains details of molecular geometry. Ring A has a distorted chair conformation (ring torsion angles $-60°$ to $+59°$) with *trans*-axial bromine atoms, ring B is a C(5) envelope [C(5) 0.66 Å from the C(6)–C(10) plane], aromatic ring C is planar, and ring D is a C(16) envelope [C(16) 0.13 Å from the C(13), C(14), C(15),C(17) plane]. The bromine-containing side chain at C(17) is maximally extended with the bromine atoms fully staggered. In the crystal structure (Figure 3) molecules are separated by normal van der Waals distances there being no untoward intermolecular contacts.

The unequivocal definition of this derivative clearly established (*a*) inversion[2] at C-17 and (*b*) that the eliminated methyl residue is C-18 as postulated.

The genesis of the 2β,3α-dibromo residue is presumably as follows. Replacement of the 3β-hydroxy group will occur with

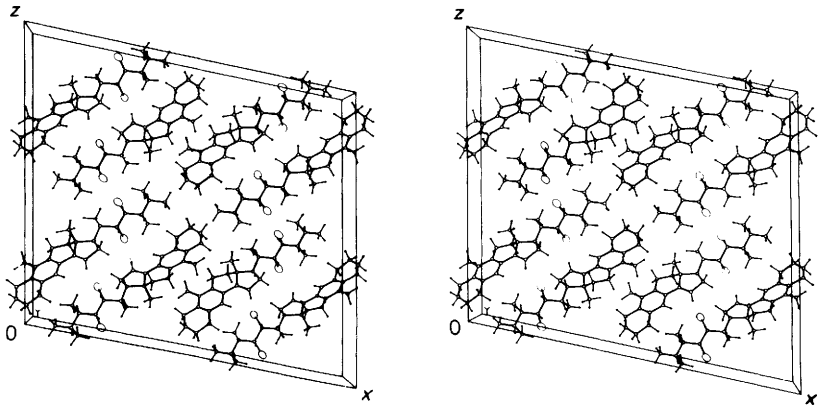
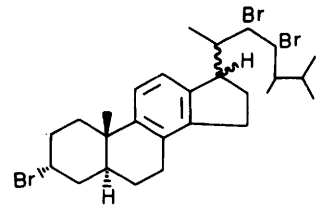
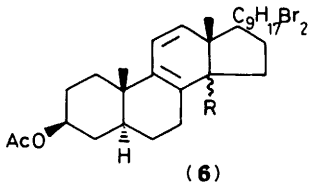


Figure 2. Stereoview of the crystal packing of $C_{28}H_{40}Br_2$ (**2**).

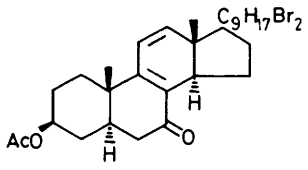
inversion to yield the 3α (axial) bromo derivative, which under the reaction conditions (presence of dimethylformamide: see Experimental section) eliminates hydrogen bromide to yield the 2,3-ene. Addition of extraneous bromine from the reagent will then yield the diaxial (2β, 3α) derivative (**4**) in accord with generally established mechanisms.



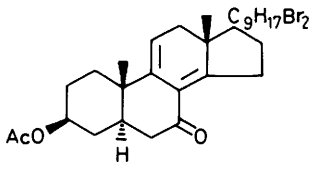
(**5**)



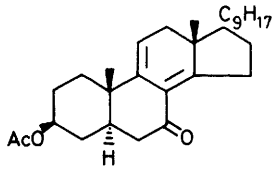
(**6**)



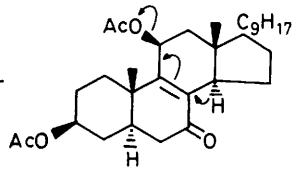
(**7**)



(**8**)



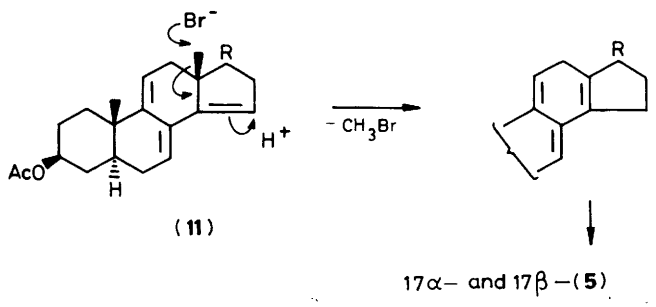
(**9**)



(**10**)

The other two products from this process were clearly the 3α,22α,23α-tribromo-18-nor-17α (and 17β) -5α-ergosta-8(9),11,13(14)-trienes (**5**). Although the data do not permit an unequivocal assignment to be made of the configuration at C-17, the similarity of the n.m.r. signals associated with the C-11 and C-12 protons in (**4**) (τ 2.75, q) to the corresponding signals (τ 2.80, q) in the epimer of m.p. 86—89 °C and the dissimilarity with the signals (τ 2.91, s) in the epimer of m.p. 200 °C, enable the tentative assignments of the side chains as 17α-(**5**) and 17β-(**5**) respectively.

The aromatisation of the tetrabromide (**1**) in chloroform with the elimination of methyl bromide (from C-18), most probably involves nucleophilic attack at C-18 on the intermediate (**11**) by Br^- as in the Scheme, and has obvious similarities to analogous



(**11**)

17α- and 17β-(**5**)

Scheme.

aromatisation[3] involving the loss of C-19. A radical mechanism is probably not involved since the addition of benzoyl peroxide (as a radical initiator) or of thymoquinone (as a radical terminator) had no effect upon the decomposition of (**1**).

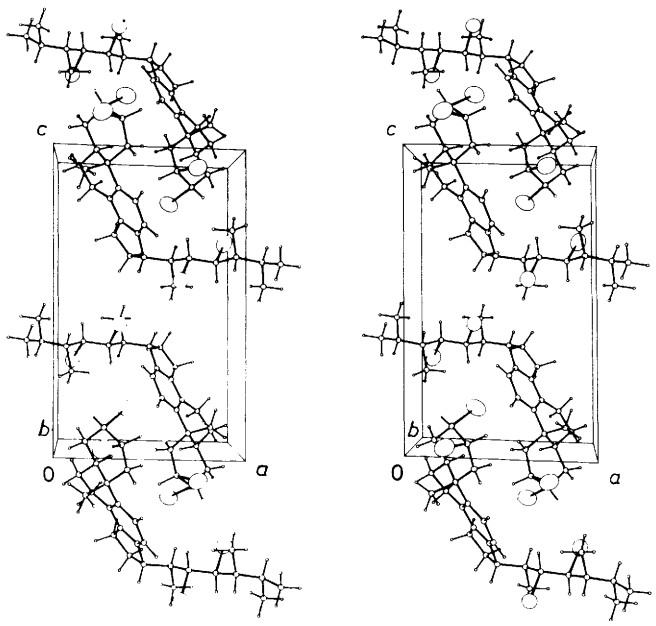


Figure 3. Stereoview of the crystal structure of $C_{27}H_{38}Br_4$ (**4**).

The delicate balance between (i) aromatisation with migration of C-18 to C-12, (ii) aromatisation of ring c with elimination of C-18 as methyl bromide, and (iii) the corresponding anthra steroid rearrangement, is illustrated by the isolation of the anthra steroid (**2**) from the same reaction mixtures.

In an alternative approach to 18-nor-8(9),11,13(14)-trienes, type (**4**), we envisaged that allylic bromination of an 8(9),11-diene of type (**6**; R = H) might furnish the bromo compound (**6**; R = Br) which could lose the elements of methyl bromide to generate type (**4**). Unfortunately, the requisite dienes are not readily available but one easily accessible, potential, synthon (**7**) had apparently been described.[4] In our repetition of this work, the general properties of the resultant dienone were in agreement with those reported[4] (see Experimental section), but the n.m.r. spectrum exhibited only one signal (τ 3.50) attributable to the presence of *one* aromatic proton, whilst the u.v. spectrum, $\lambda_{max.}$ 294 nm, was inconsistent with that calculated, $\lambda_{max.}$ 324 nm. It thus appears that this dienone should be represented by (**8**), a structure which is compatible with (*a*) the physical data, (*b*), its debromination (see Experimental section) to the known[5] dienone (**9**), and (*c*) the derivation[4] of (**8**) from (**10**) by treatment with acid.

Experimental

Light petroleum refers to the fraction of b.p. 60—80 °C. N.m.r. spectra were recorded at 60 MHz using a Perkin-Elmer R12A spectrometer or at 250 MHz with a Bruker WM 250 (by courtesy of King's College, London), in deuteriochloroform.

H.p.l.c. was performed using a Constrametric III pump with a variable u.v. detector and valve injector fitted with a 20 μl loop. Analyses were performed with a 25 × 0.32 cm column packed with 5μ Spherisorb ODS, mobile phase, 92:8 methanol–water, flow rate 2 ml/min., u.v. detector 220 nm.

Samples (*ca.* 50 mg) were partially purified by p.t.l.c., on silica prior to injection (in 5-ml portions of chloroform).

Decomposition of 7α,11α,22α,23α-*Tetrabromo*-5α-*ergost*-8-*en*-3β-*yl Acetate* (**1**) *in Chloroform: Quantitative Measurement of Methyl Bromide.*—A solution of the tetrabromide[2] (12.0 g, 14.8

Table 2. Quantitative determination of methyl bromide

Standard			Reaction		
CH_3Br peak	$CHCl_3$ peak	Ratio	CH_3Br peak	$CHCl_3$ peak	Ratio
268 mg	425 mg	0.631	27 mg	443 mg	0.0603
292	406	0.719	36	631	0.0571
301	408	0.738	20	287	0.0697
339	445	0.762	31	524	0.0592
			24	420	0.0599
	Average	0.713		Average	0.0599

mmol) in chloroform (120 ml) was added to a flask fitted with a rubber septum and a trap containing solid sodium hydroxide. The closed system was allowed to stand for 3 weeks at room temperature (*ca.* 20 °C). A standard solution of methyl bromide (3.721 g) in chloroform (40.297 g, 27.02 ml) was prepared. Alternate samples of the green reaction mixture and of the standard were injected into a g.l.c. column at 54 °C. The peaks caused by the methyl bromide and the chloroform were well separated and were cut out of the chart paper and weighed. The results are shown in Table 2, and from these data the concentration of CH_3Br is thus 0.0599/0.713 that of the standard. Thus, it contained 1.38 g of methyl bromide (14.5 mmol). The yield is 92%. In a separate experiment the methyl bromide was collected and identified on the basis of its n.m.r. spectrum (τ 7.36, s, CH_3) and mass spectrum (Found: M^+, 93.9416; $CH_3{}^{79}Br$ requires *M*, 93.9419).

General Experimental Protocol.—The following conditions are representative of the many variations carried out on the method.

(a) 22α,23a-*Dibromo*-10-*methyl*-19-*noranthraergosta*-5,7,9(10),14-*tetraene* (**2**).—A solution of the tetrabromide (**1**) (6.8 g) in pure chloroform (500 ml) was kept for 3 days at room temperature in the dark and then washed with water, aqueous sodium hydrogen carbonate, and water, and then dried and evaporated under reduced pressure to yield a yellow gum. A solution of this in benzene was filtered through silica and chromatographed on alumina (Spence Type H, 150 g). Elution with light petroleum followed by 5% ether–light petroleum gave 22α,23α-*dibromo*-10-*methyl*-19-*noranthraergosta*-5,7,9(10),14-*tetraene* (0.1 g) as plates, m.p. 217—222 °C from dichloromethane–methanol: $\lambda_{max.}$(chloroform) 266 nm (log ε 3.87); τ 2.72 (1 H, s, 7-H), 4.0 (1 H, 15-H), 5.5 (2 H, m, 22-, 23-H), and 7.85 (3 H, s, Ar-Me) (Found: C, 62.8; H, 7.6%; M^+, 536. $C_{28}H_{40}Br_2$ requires C, 62.7; H, 7.5%; *M*, 536).

(b) 2β,3α,22α,23α,-*Tetrabromo*-18-*nor*-5α-17-*isoergosta*-8,11,13-*triene* (**4**).—A solution of crude product (7 g) obtained as in (*a*) was separated by chromatography from benzene on alumina (Spence Type H). The fraction (2 g), eluted with 8% ether in light petroleum, was shown by n.m.r. to be chiefly material exhibiting a multiplet at τ 2.8 (Ar-H's). This fraction was hydrolysed with warm methanolic potassium hydroxide during 2 h, and the hydrolysate, in dimethylformamide (20 ml), added to triphenylphosphine dibromide (8 g) dissolved in dimethylformamide (25 ml) at room temperature (nitrogen). After 18 h the product was dissolved in 2.5% benzene in light petroleum (600 ml) and the solution filtered through silica. The product was separated by repeated t.l.c. (on a 1-g sample) on silica from light petroleum to yield four fractions on the basis of their n.m.r. spectra: (**1**) 0.2 g, τ 3.05, 7.7 (s, 12-Me); (**2**) 0.2 g, τ 2.8 (q_{AB}, *J* 8 Hz); (**3**) 0.1 g; τ 7.7 (s, 12-Me); (**4**) 0.1 g, τ 2.85 (q_{AB}, *J* 8 Hz). Each fraction was then further purified by h.p.l.c., when (**4**) separated from acetone–dichloromethane–methanol as large prisms, m.p. 152—153 °C of 2β,3α,22α,23α-*tetrabromo*-18-*nor*-5α-17-*isoergosta*-8,11,13-*triene*, with τ 2.75 (2 H, q_{AB}, *J* 7.9 Hz, 11-, 12-H), 5.1 (2 H, m, 3-, 2-H), and 5.5 (2 H, s, 22-, 23-H) (Found: C, 47.6; H, 5.9%; M^+, 677.9711. $C_{27}H_{38}Br_4$ requires C, 47.5; H, 5.6%; *M*, 677.9707).

Similar treatment of fraction (2) gave 3α,22α,23α-*tribromo*-18-*nor*-5α-17α-*ergosta*-8,11,13-*triene* which separated from acetone–methanol as needles, m.p. 86—89 °C (Found: M^+, 600. $C_{27}H_{39}Br_3$ requires *M*, 600). With τ 2.80 (2 H, q_{AB}, *J* 7.9 Hz, 11-, 12-H), 5.2 (1 H, m, 3β-H), and 5.49 (2 H, s, 22-, 23-H) (Found: C, 53.3; H, 6.5%; M^+, 600. $C_{27}H_{39}Br_3$ requires C, 53.8; H, 6.5%; *M*, 600).

Similarly fraction (3) gave 3α,22α,23α-*tribromo*-18-*nor*-5α,-17β-*ergosta*-8,11,13-*triene* as needles, m.p. 200—203 °C from acetone–methanol (Found: M^+, 600. $C_{27}H_{39}Br_3$ requires *M*, 600), with τ 2.91 (2 H, 11-, 12-H), 5.21 (1 H, m, 3β-H), 5.47 (2 H, s, 22-, 23-H), 6.9 (1 H, m, 17-H), and 7.3 (4 H, m, 7-, 15-H's) (Found: C, 54.4; H, 6.5%; M^+, 600. $C_{27}H_{39}Br_3$ required C, 53.8; H, 6.5%; *M*, 600).

3α,22α,23α-*Tribromo*-12-*methyl*-18-*nor*-5α-*ergosta*-8,11,13-*triene*.—A solution of 22,23-dibromo-12-methyl-18-nor-5α-ergosta-8,11,13-trien-3β-ol (0.25 g) in dimethylformamide (1 ml) was added to a solution of triphenylphosphine dibromide (0.65 g) in dimethylformamide (5 ml) at −5 °C. After 0.5 h the product was isolated and purified from acetone–methanol as needles, m.p. 209—211 °C (Found: C, 54.6; H, 6.7%; M^+, 614. $C_{28}H_{41}Br_3$ requires C, 54.5; H, 6.7%; *M*, 614).

3α-*Acetoxy*-22,23-*dibromoergosta*-8(14),9(11)-*dien*-7-*one*.—Prepared as previously described,[4] this ketone had m.p. 248 °C (decomp.) (lit.[4] 263 °C); $\lambda_{max.}$ 223 (log ε 4.16) and 294 nm (368) [lit.,[4] 224 (log ε 4.26) and 296 nm (3.78)]; τ 3.5 (1 H, m, 11-H), 5.3 (1 H, m, 3-H), 5.6 (2 H, m, 22-, 23-H), 7.95 (3 H, s, OCOMe) (Found: M^+, 612. Calc. for $C_{30}H_{44}Br_2O_3$: *M*, 612).

3α-*Acetoxyergosta*-8(14),9(11),22-*trien*-7-*one*.—Prepared from a solution in benzene (30 ml) of the preceding ketone (0.23 g) and zinc dust (3 g), during 6 h, at room temperature this ketone (0.15 g) formed plates, m.p. 188—190 °C, from methanol (lit.,[5] m.p. 187—189 °C); $[\alpha]_D^2$ −47.6° (lit.,[5] −47°); τ 3.6 (1 H, m, 11-H), 4.75 (2 H, m, 22-, 23-H), 5.3 (1 H, m, 3-H), and 7.97 (3 H, s, OCOMe); $\lambda_{max.}$ 222 (log ε 4.17) and 297 nm (3.70) [lit.,[5] $\lambda_{max.}$ 300 nm (log ε 3.70].

Crystal Structure Analyses of Compounds (**2**) *and* (**4**).—Crystals of compound (**2**) were colourless thin plates, those of (**4**) were colourless parallelepipeds. Preliminary cell data were obtained from Weissenberg and precession photographs; accurate cell date for both (**2**) and (**4**) were obtained in each case from a least-squares treatment of the setting angles of 12 reflections measured on a diffractometer.

Crystal data for (**2**). $C_{28}H_{40}Br_2$, M = 536.5, monoclinic, a = 31.38(2), b = 5.918(2), c = 28.469(9) Å, β = 102.20(1)°, U = 5 167 Å^3, Z = 8, D_c = 1.38 g cm^{-3}, $F(000)$ = 2 224. Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 31 cm^{-1}. Space group $F2$ (non standard setting of $C2$, chosen to avoid a large β angle in $C2$) from systematic absences (*hkl* absent if $h + k$, $k + l$, $l + h$ are odd) and from the known optical activity of the sample (which rules out other possible space groups such as $C2/m$ or Cm types).

Crystal data for (**4**). $C_{27}H_{38}Br_4$, M = 682.2, monoclinic, a = 10.512(2), b = 7.682(1), c = 17.148(2) Å, β = 91.59(2)°, U = 1 384.1 Å, Z = 2, D_c = 1.64, $F(000)$ = 680, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 58 cm^{-1}. Space group $P2_1$ or $P2_1/m$ from systematic absences (*0,k,0* when *k* odd). $P2_1$ from structure analysis and the known optical activity of the compound.

For both (**2**) and (**4**) the intensities of all reflections $+h$, $\pm k$

Table 3. Final fractional co-ordinates for 22,23-dibromo-10-methyl-19-noranthraergosta-5,7,9(10),14-tetraene

Atom	*x/a*	*y/b*	*z/c*
Br(1)	2 747(1)	0*	4 639(1)
Br(2)	2 902(1)	4 968(9)	3 421(1)
C(1)	509(7)	−3 254(42)	1 137(7)
C(2)†	160(14)	−2 758(94)	697(15)
C(2)′†	51(21)	−3 394(109)	808(22)
C(3)′†	−122(18)	−1 565(95)	733(17)
C(3)†	−295(13)	−2 214(78)	888(15)
C(4)	−266(6)	−108(61)	1 182(7)
C(5)	213(5)	−247(43)	1 560(5)
C(6)	539(7)	−1 572(38)	1 534(7)
C(7)	936(6)	−1 409(39)	1 875(7)
C(8)	1 011(5)	295(45)	2 218(5)
C(9)	678(6)	1 795(35)	2 257(6)
C(10)	271(6)	1 609(36)	1 920(6)
C(11)	737(7)	3 588(40)	2 629(7)
C(12)	1 221(6)	4 011(35)	2 866(7)
C(13)	1 472(6)	1 754(35)	3 014(6)
C(14)	1 438(5)	366(42)	2 566(5)
C(15)	1 798(6)	−573(32)	2 534(6)
C(16)	2 173(6)	−4(58)	2 962(6)
C(17)	1 977(6)	2 232(36)	3 155(6)
C(18)	2 179(6)	2 632(40)	3 704(7)
C(19)	2 018(5)	4 676(40)	3 905(6)
C(20)	2 693(6)	2 449(39)	3 782(6)
C(21)	2 941(6)	2 620(40)	4 316(6)
C(22)	3 436(6)	2 605(43)	4 385(6)
C(23)	3 606(7)	720(45)	4 124(8)
C(24)	3 679(7)	2 701(44)	4 916(7)
C(25)	4 153(7)	3 105(50)	4 968(8)
C(26)	3 500(7)	4 424(43)	5 183(8)
C(27)	1 277(5)	589(36)	3 384(6)
C(28)	−81(7)	3 221(44)	1 961(7)

* Held to fix the origin. † Population parameter 0.5 to account for disorder.

Table 4. Final fractional co-ordinates (Br × 10^4; C × 10^3) with estimated standard deviations for 2β,3α,22,23-tetrabromo-18-nor-17-isoergosta-8(9),11,13(14)-triene (**4**)

Atom	*x/a*	*y/b*	*z/c*
Br(2)	7 478(2)	−10 233(5)	−642(1)
Br(3)	6 245(3)	−5 000(0)	−1 603(1)
Br(22)	3 478(2)	−6 412(6)	4 261(1)
Br(23)	894(2)	−2 396(6)	2 965(2)
C(1)	621(2)	−736(3)	16(1)
C(2)	656(2)	−801(2)	−64(1)
C(3)	740(2)	−673(3)	−110(1)
C(4)	834(2)	−573(2)	−60(1)
C(5)	778(2)	−498(3)	15(1)
C(6)	868(2)	−379(3)	61(1)
C(7)	799(2)	−290(3)	126(1)
C(8)	706(2)	−396(3)	165(1)
C(9)	665(2)	—557(3)	138(1)
C(10)	723(2)	—648(2)	66(1)
C(11)	582(2)	—656(3)	183(1)
C(12)	533(2)	—599(4)	251(1)
C(13)	562(2)	−429(3)	276(1)
C(14)	649(2)	−334(3)	234(1)
C(15)	680(2)	−168(3)	275(1)
C(16)	598(2)	−156(4)	344(1)
C(17)	528(2)	−338(3)	350(1)
C(19)	831(2)	−770(3)	97(1)
C(20)	378(2)	−301(3)	359(1)
C(21)	354(4)	−204(5)	439(2)
C(22)	293(2)	−461(3)	352(1)
C(23)	152(2)	−437(3)	364(1)
C(24)	60(2)	−596(4)	348(1)
C(25)	82(3)	−664(4)	266(2)
C(26)	−79(2)	−570(3)	362(1)
C(27)	−96(2)	−465(5)	440(2)
C(28)	−152(3)	−738(5)	364(2)

and $\pm l$ with $2 < \theta < 20°$ were measured on a Hilger and Watts Y290 diffractometer in our usual way,[6] both the $+k$ and $-k$ reflections being measured to allow us to determine the absolute configuration. The intensities were corrected for Lorentz and polarisation factors but not for absorption. F(**2**) 2 419 reflections were measured of which 1 535 had $I > 3\sigma(I)$. Initially, the k and $-k$ reflections were averaged; for the final calculations for computational convenience, only the 853 reflections with $+k$ and $I > 3\sigma(I)$ were used. The corresponding numbers for (**4**) are 2 489 unique reflections measured, 2 092 with $I > 3\sigma(I)$, and 1 136 with $+k$ and $I > 3\sigma(I)$.

Structure Analyses of (**2**) *and* (**4**).—Both structures were solved by the heavy-atom method; the co-ordinates of the two bromine atoms in (**2**) and the four bromine atoms in (**4**) were deduced from their three-dimensional Patterson functions. For (**2**), the two Br atoms are separated by 0.5 in y and this inevitably led to pseudo-symmetry problems in the first heavy-atom phased electron-density maps; there were no such pseudo-symmetry problems with (**4**). For both molecules full-matrix least-squares refinement [7] with isotropic thermal parameters for the Br and C atoms proceeded with the averaged data sets and no allowance for anomalous dispersion of bromine. Difference syntheses computed at various stages of the refinement showed maxima consistent with most of the expected hydrogen atoms, in positions close to those expected.

To determine the absolute stereochemistry unequivocally, the structure amplitude set for each molecule, with unmerged k and $-k$ reflections, was used and anomalous dispersion corrections for the bromine atoms were made. In each case, two separate sets of refinement calculations were made for structures with general co-ordinates x, y, z and $x, -y, z$. These refinement cycles converged with R-factors of 0.078 and 0.072 for the x, y, z, and $x, -y, z$ models for (**2**), and 0.071 and 0.068 for the corresponding models for (**4**). In each case, the structure with the $x, -y, z$ set of co-ordinates was chosen as having the correct absolute configuration; these are also the configurations expected on chemical grounds. For the final cycles of refinement, for computational convenience and because of financial constraints, only the observed data with $h, +k, \pm l$ were used. In the case of (**2**) there was clear indication of disorder affecting the atoms C(2) and C(3) in ring A, with each atom disordered over two sites with equal occupancy above and below the C(1), C(4), C(5), and C(6) plane. This had been suspected because of abnormally large temperature factors found for these atoms during isotropic refinement. In the final rounds of calculations this disorder was allowed for, the hydrogen atoms in the structure were placed from geometrical considerations, an overall isotropic temperature factor was refined for the hydrogen atoms, the carbon atoms were constrained to isotropic motion, and the Br atoms allowed to vibrate anisotropically. At convergence $R = 0.051$ and $R_w = (\Sigma w\Delta^2/\Sigma wFo^2)^{\frac{1}{2}} = 0.055$.

In the final rounds of calculations for (**4**), the carbon and bromine atoms were allowed anisotropic motion and the hydrogen atoms were allowed for but not refined. At convergence $R = 0.052$ and $R_w = 0.055$.

For both structures, final difference maps were devoid of chemically significant features. Weights in the refinements were based on the counting statistics, and the scattering factors for C and Br were taken from ref. 8, those for H from ref. 9 and anomalous dispersion data for Br from ref. 10.

The final fractional co-ordinates for (**2**) and (**4**) are in Tables 3 and 4 respectively. A list of molecular dimensions, thermal parameters, and hydrogen coordinates has been treated as a Supplementary publication (SUP No. 56217 (8 pp.).* The *structure* factors are available on request from the editorial office.

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* For details of the Supplementary publications scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1.

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