Extractives from *Pseudowintera colorata*. Part V.[1] A New Sesquiterpene Lactone, Colorata-4(13),8-dienolide

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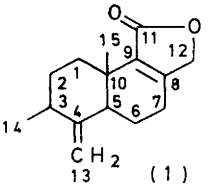
The structure of colorata-4(13),8-dienolide, a new sesquiterpene lactone isolated from the shrub *Pseudowintera colorata*, has been elucidated.

THE volatile oil of *Pseudowintera colorata* (pepper tree), a shrub endemic to New Zealand, was first examined by Finlay,[2] who identified *p*-mentha-1(7),2-diene in the terpene fraction, and latter by Melville and Levi,[3] who isolated pin-2-ene, (+)-*p*-mentha-1,8-diene, and (±)-*p*-mentha-1,8-diene as well as terpene alcohols and esters and made a preliminary study of the sesquiterpene fraction. By a precise fractional distillation, Corbett and his co-workers [4,5] isolated *ca.* 34 compounds from the oil, including the sesquiterpene ketone cyclocolorenone.[5] The investigation of this shrub has now been extended to the extractives from the bark, from which a new sesquiterpene lactone, colorata-4(13),8-dienolide (1), has been isolated. This butenolide has been shown to be a bicyclofarnesol derivative, of which drimenin (2), isodrimenin (3) and confertifolin (4) are typical examples.[6] *Pseudowintera colorata* is botanically closely related to the South American *Drimys* species from which these compounds were first isolated.

The i.r. and u.v. spectra of the dihydro-derivative, colorat-8-enolide (5), are closely similar to those of isodrimenin (3) (Table 1) and show the presence of an αβ-unsaturated γ-lactone (butenolide) unit. In addition the i.r. spectrum of (1) (in Nujol) contains absorption



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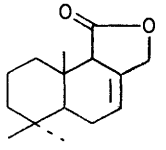

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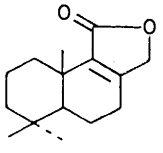

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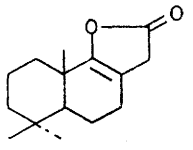


(4)

from an exocyclic methylene group (1640 and 885 cm^{-1}). The ^1H n.m.r. spectrum contains signals for one tertiary (δ 0.91) and one secondary methyl group (δ 1.10 and 1.04),

[1] Part IV, R. E. Corbett and H. Young, *Austral. J. Chem.*, 1963, **16**, 250.
[2] H. J. Finlay, *New Zealand J. Sci. Technol.*, 1926, **8**, 107.
[3] J. Melville and A. A. Levi, *J. Soc. Chem. Ind.*, 1932, **51**, 210T.
[4] R. E. Corbett and P. K. Grant, *J. Sci. Food. Agric.*, 1958, **9**, 733; R. E. Corbett, *ibid.*, 1962, **13**, 158.
[5] R. E. Corbett and R. M. Speden, *J. Chem. Soc.*, 1958, 3710.
[6] H. H. Appel, J. D. Connolly, K. H. Overton, and R. P. M. Bond, *J. Chem. Soc.*, 1960, 4685.

and an exocyclic methylene group (δ 4.62 and 4.82). Because the n.m.r. spectra of compounds (1) and (5) do not contain any other vinylic proton absorption the double bond of the butenolide group must be fully substituted. The sharp peak at 780 cm^{-1} (Nujol) in the i.r. spectra of (1) and all its derivatives in which the butenolide unit remains intact appears to be characteristic of a double bond in this particular type of butenolide unit.[6]

methyl groups was the same as when $CDCl_3$ was the solvent. Substantial benzene-induced changes in the chemical shifts of methyl substituents at C-1, C-2, and C-4 would be expected[8,9] but methyl groups at C-3 would lie in a plane drawn through C-11 at right angles to the carbon–oxygen bond, and a benzene-induced change in chemical shift would not be expected. The benzene induced shift of 0.14 p.p.m. in the signal of the

TABLE 1

I.r. and u.v. spectral characteristics of corresponding derivatives of colorata-4(13),8-dienolide (1) and isodrimenin (5)

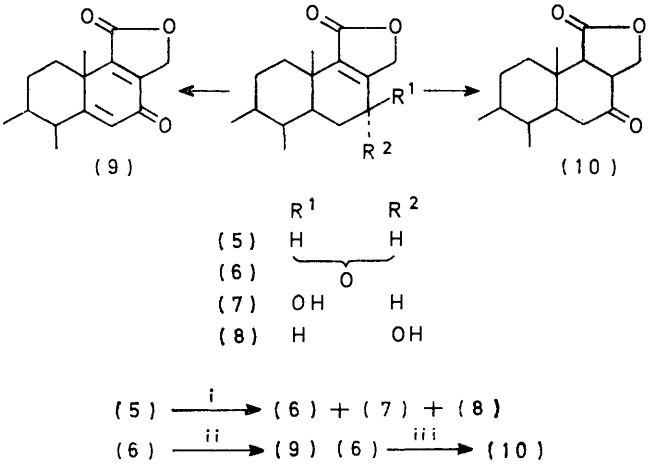
	$\nu_{max.}(CCl_4)/cm^{-1}$	$\lambda_{max.}(EtOH)/nm$	$\varepsilon_{max.}$
Colorata-4(13),8-dienolide (1)	1 751, 1 662	219.5	16 800
Colorat-8-enolide (5)	1 762, 1 668	217.0	14 150
Isodrimenin (3) [6]	1 766, 1 671	218.0	10 000
7-Oxocolorat-8-enolide (6)	1 775, 1 697	248.5	11 880
7-Oxoisodrimenin [6]	1 774, 1 690	247.0	10 600
7-Oxocolorata-5,8-dienolide (9)	1 772, 1 685, 1 654	249.0	13 430
7-Oxodehydroisodrimenin [6]	1 773, 1 682, 1 651	248.0	14 800
7-Oxocoloratanolide (10)	1 780, 1 710	283.0	32
7-Oxodihydroisodrimenin [6]	1 781, 1 716	282.0	30
7-Oxodihydroisodrimenin [7]	1 778, 1 712		

The location of the lactonic carbonyl group at C-11 as in isodrimenin (3) rather than at C-12 as in confertifolin (4) follows from the complete resistance of the 8,9-ethylenic linkage to hydrogenation, even with Adams catalyst in the presence of perchloric acid, and from the singlet nature of the signal from the methylene group of the butenolide in the n.m.r. spectra of (1) [δ 4.82 (2 H, s, CH_2 of butenolide)] and all its derivatives in which the unit remains intact. If the carbonyl and methylene groups of the butenolide system were at C-12 and C-11 respectively, as in confertifolin (4), the 8,9-ethylenic linkage would be susceptible to hydrogenation,[6] and the methylene n.m.r. signal would appear as a multiplet because of homoallylic coupling with the two hydrogen atoms at C-7. The singlet nature of the C-12 methylene signal also excludes the possibility of a hydrogen atom at C-10 and is in harmony with the presence of a methyl group at this position.

Ring B of structure (1) was shown to be identical with ring B of isodrimenin (3) as follows. Application of a series of degradations (Scheme 1) which had been applied to isodrimenin (3) to colorat-8-enolide (5) gave products with spectral characteristics identical, within experimental error (note variation in reported absorption of, for example, 7-oxodihydroisodrimenin [7]), with those reported for the corresponding isodrimenin derivatives (Table 1). The close similarity in the spectral characteristics of the derivatives listed indicates not only identical structures for rings B of structures (1) and (3) but also identical stereochemistry at the junction with ring A.

A methyl group and a methylene group have to be accommodated in ring A, which in the absence of any other spectrally definable features is required by the molecular formula to be six-membered. When the n.m.r. spectrum of colorat-8-enolide (5) was measured in benzene the chemical shift of one of the secondary

other secondary methyl group (Table 2) is identical with that reported for the 4α- and 4β-methyl groups of isodrimenin (3).[9a] These observations indicated that secondary methyl groups are located at C-3 and C-4 in colorat-8-enolide (5). The small benzene-induced shift (+0.07 p.p.m.) in the signal from the 10β-methyl group



SCHEME 1 Reagents: i, CrO_3–AcOH; ii, SeO_2–AcOH; iii, Zn–AcOH

in (5) (Table 2) is predictably similar to that of the 10β-methyl group in isodimerin (3).[9a] The chemical shift of the 10β-methyl group in (1) is not affected when the solvent is changed from $CDCl_3$ to C_6D_6 (Table 4). This too is predictable since the substituent effect of the C-11 carbonyl group [$\delta(CDCl_3) - \delta(C_6D_6)$] has been shown to be +0.07 p.p.m. whereas that of a 4-methylene group in a cholestane structure is −0.05 p.p.m.[9b]

The diol (11) was obtained in high yield and was the only product of the osmylation of compound (1). α-Face attack would be predicted on a C-4 methylene group

[7] C. J. W. Brooks and G. H. Draffan, *Tetrahedron*, 1969, **25**, 2887.

[8] N. S. Bhacca and D. W. Williams, *Tetrahedron*, 1965, **21**, 2021.

[9] (*a*) J. D. Connolly and R. McGrindle, *Chem. and Ind.*, 1965, 2067; (*b*) M. Fetizon, Jean-Claude Gramain and Issam Hanna, *Bull. Soc. chim. France*, 1971, 1388.

and the small change in the chemical shift of the 10β-methyl signal (−0.05 p.p.m.) is consistent with the replacement of a 4β-methyl group [in (5)] by a 4β-hydroxymethyl group [in (11)]. Cleavage of the α-glycol group in (11) under conditions which would preclude isomerization at an adjacent carbon atom gave the cyclohexanone (12) [$\nu_{max.}$ 1 708 cm^{-1} (C=O)]. This ketone proved unusually unreactive, and failed to undergo the Baeyer–Villiger reaction under any of the usual conditions. Reduction of the ketone (12) with sodium borohydride took place exclusively from the α-face and gave a quantitative yield of the axial alcohol (13). The change in the chemical shift of the 10β-methyl group from δ 0.96 in (12) to δ 1.25 in (13) is diagnostic of an axial 4β-hydroxy-group in (13).

TABLE 2

Δ Values[δ($CDCl_3$) − δ(C_6D_6)] for methyl resonances in compounds (3) and (5)

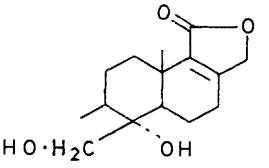
Compound	3-Me	4-Me(s)	10-Me
Isodrimenin (3) [9]		+0.13, +0.14	+0.06
Colorat-8-enolide (5)	0.00	+0.14	+0.07

TABLE 3

Changes in the 10-Me chemical shifts between epimeric 4-oxo-5α*H*- and 4-oxo-5β*H*-compounds

Compound	$\delta_{10\text{-Me}}$ in CCl_4	Difference (p.p.m.)
4-Oxo-5α-cholestane [13a]	0.745	0.368
4-Oxo-5β-cholestane [13a]	1.113	
4-Oxo-5α-androstane [13b]	0.73	0.36
4-Oxo-5β-androstane [13b]	1.09	
4-Oxo-17β-propionyloxy-5α-androstane [13a]	0.757	0.366
4-Oxo-17β-propionyloxy-5β-androstane [13a]	1.123	
4-Oxo-13-norcolorat-8-enolide (12)	0.96	0.33
5β*H*-4-Oxo-13-norcolorat-8-enolide (16)	1.29	
4-Oxo-13-norcolorat-8-enolide (12)	0.96	0.38
4-Oxo-13-nor-3β*H*,5β*H*-colorat-8-enolide (17)	1.34	

Enol acetylation of the ketone (12) gave two isomers (Scheme 2). Both the enol acetate (14) [δ 1.52 (3 H, s, CH_3–C=C–OAc)], the major product, and the enol acetate (15) [δ 1.52 and 1.54 (3 H, d, CH_3–C=C–OAc)], the minor product, contain vinylic methyl groups. The oxo-group must be adjacent to the secondary methyl group, as in the proposed structure, and to account for the two isomers, to a ring junction. The oxo-group in (12) must be at C-4 and the secondary methyl group at C-3. The two 3,4-enol acetates, (14) and (15), must be isomeric at the AB ring junction. A vinylic C(3)–CH_3 bond in a compound containing a 3,4-double bond is at 90° to the C(5)–H bond if rings A and B are *trans*-fused and would exhibit homoallylic coupling, giving a doublet (*J ca.* 2 Hz) [10] in the n.m.r. spectrum. On the other



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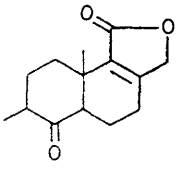

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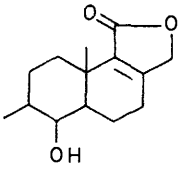


(13)

TABLE 4

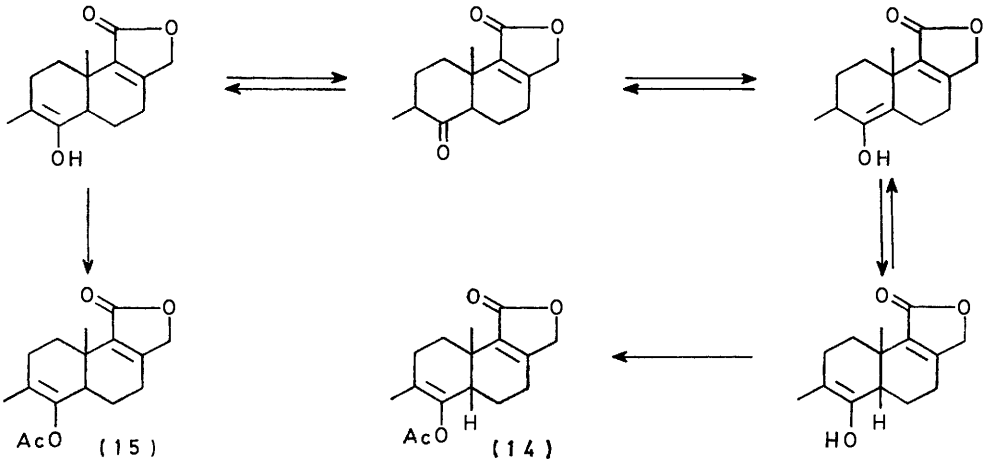
Chemical shifts (δ)† of methyl groups (solvent $CDCl_3$)

Compound	C-3	C-4	C-10
Isodrimenin (3)		0.84, 0.88	1.08
Colorata-4(13),8-dienolide (1)	(1.04, 1.10)		0.91
	(0.96, 1.02) *		0.91 *
Colorat-8-enolide (5)	(0.77, 0.85)	(0.85, 0.91)	1.10
	(0.77, 0.85) *	(0.71, 0.77) *	1.03
7-Oxocolorat-8-enolide (6)	(0.85, 0.92)	(0.90, 0.96)	1.26
7β-Hydroxycolorat-8-enolide (7)	(0.96, 1.01)	(1.01, 1.08)	1.21
7α-Hydroxycolorat-8-enolide (8)	(0.92, 0.98)	(1.01, 1.08)	1.08
7-Oxocolorata-5,8-dienolide (9)	(0.97, 1.03)	(1.17. 1.24)	1.53
7-Oxocoloratanolide (10)	(0.79, 0.86)	(0.90, 0.96)	0.86
4α,13-Dihydroxycolorat-8-enolide (11)	(0.99, 1.05)		1.05
4-Oxo-13-norcolorat-8-enolide (12)	(1.00, 1.07)		0.96
	(0.96, 1.03) *		0.82 *
4-Oxo-13-nor-5β*H*-8-enolide (16)	(1.05, 1.12)		1.29
	(0.91, 0.98) *		1.06 *
4-Oxo-13-nor-3β*H*,5β*H*-colorat-8-enolide (17)	(0.94, 1.01)		1.34
	(0.87, 0.94) *		1.06 *
4β-Hydroxy-13-norcolorat-8-enolide (13)	(0.95, 1.01)		1.25
4-Acetoxy-13-nor-5β*H*-colorata-3,8-dienolide (14)	1.52		1.31
4-Acetoxy-13-nor-colorata-3,8-dienolide (15)	(1.52, 1.54)		1.09
Colorata-2,8-dienolide (18)	1.68	(1.05, 1.12)	1.02
Colorata-4,8-dienolide (19)	(0.99, 1.06)	1.67	1.29
4α,13-Epoxycolorat-8-enolide (20)	(0.74, 0.81)		1.09
Diol (21)	(0.73, 0.80)	(0.84, 0.90)	0.93
Diol (22)	(0.67, 0.74)	(0.83, 0.89)	1.01
Diol (23)	(0.70, 0.77)	(0.83, 0.89)	0.77

* Measured in C_6D_6. † Parentheses indicate a doublet.

[10] N. S. Bhacca and D. H. Williams, ' Applications of N.M.R. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, p. 110.

hand, if the AB ring junction is *cis* the corresponding angle is *ca.* 0° if the molecule adopts a non-steroid like conformation, but 90° (resulting in homoallylic coupling) if a steroid-like conformation is adopted. To account for the n.m.r. data, compound (14) must have a *cis* AB ring junction and a non-steroidal conformation, whereas (15) is considered to be the *trans*-AB epimer. The 10β-methyl

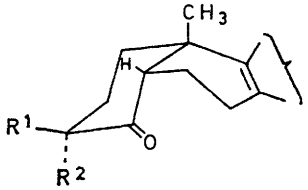


SCHEME 2 Reagent: Ac_2O–TsOH

resonances of the two compounds [(14), δ 1.31; (15), δ 1.09] are consistent with these structural requirements. If Zurcher's rules [11] are applied, with colorat-8-enolide (5) as the parent compound, a value of δ 1.087 is predicted for the 10β-methyl group in (15) [1.10 — 0.03 (4β-Me) — 0.025 (3,4-C=C) + 0.042 (4α-OAc) = 1.087],[7] and this is in good agreement with the observed value. The values used in the calculation for substituent effects are approximate only, that for the 4β-methyl group being taken from the data for 5α-cholestane and 4β-methyl-5α-cholestane.[12] Figures do not appear to have been published for the effect of a 3,4-double bond on a 10β-methyl group in a cholestane structure, but the substituent effect of a 6,7-double bond, which is in a similar steric relationship to a 10β-methyl group in a *trans*-AB ring system, normally causes an upfield shift of 0.025 p.p.m.[11] The steric relationship of the vinylic acetate at C-4 to the 10β-methyl group is similar to that of a 4α- or 6α-acetoxy-group, and the substituent effect should be of the same order. When extrapolations from a cholestane-like structure are made, it should be noted that the effect of substituents in ring B is smaller than the effect of corresponding groups in ring A (4β-OH, +0.267; 6β-OH, +0.225; 4β-OAc, +0.225; 6β-OAc, +0.183; 6α-OAc, +0.042 p.p.m.).[11]

In the non-steroid-like structure proposed for (14) the 10β-methyl group is in the same steric relationship to the 4-acetoxy-3-ene unit as it is in the enol acetate (15), and the substituent effect of this group will be the same. On the other hand the 10β-methyl group in (14) is much further into the deshielding zone of the butenolide group than it is in (15) and a considerable downfield shift in the signal might be expected. The value of the 10β-methyl resonance (δ 1.31) is consistent with these observations. From the ratio of *cis*- to *trans*- (4 : 1) epimers, it is clear that the *cis*-non-steroid-like enol acetate (14) is the more stable. Apparently the non-steroid-like *cis*-structure (14), which is more open, is more sterically favoured than the inverted V-shaped, folded-in, conformation resulting from a steroid-like ring fusion.

With ethanolic potassium hydroxide, the ketone (12) gave two isomers, the ketones (16) and (17), in the ratio 3 : 2. When compound (16) was equilibrated with ethanolic potassium hydroxide, or when the enol acetate (14) was hydrolysed with dilute sulphuric acid, an identical mixture of (16) and (17) was obtained. Four isomers are possible if the oxo-group is adjacent to a ring junction and to a methyl group; any other arrangement of oxo-group and methyl group in ring A would give rise to two isomers only. The isolation of the three isomers further supports formula (1) for colorat-4(13),8-dienolide.



	R^1	R^2
(16)	Me	H
(17)	H	Me

A comparison of the chemical shifts of the C-10 methyl groups in the 5α- and 5β-4-oxocholestanes,[13a] 4-oxo-androstanes,[13b] and 4-oxo-17β-propionyloxyandrostanes [13a] (Table 3) shows that when a *trans*-ring junction is converted into a *cis*- the 10β-methyl signal undergoes a

[11] Ref. 10, pp. 19—21.

[12] J.-C. Jacquesy, R. Jacquesy, J. Levisalles, J.-P. Pete, and H. Rudder, *Bull. Soc. chim. France*, 1964, 2224.

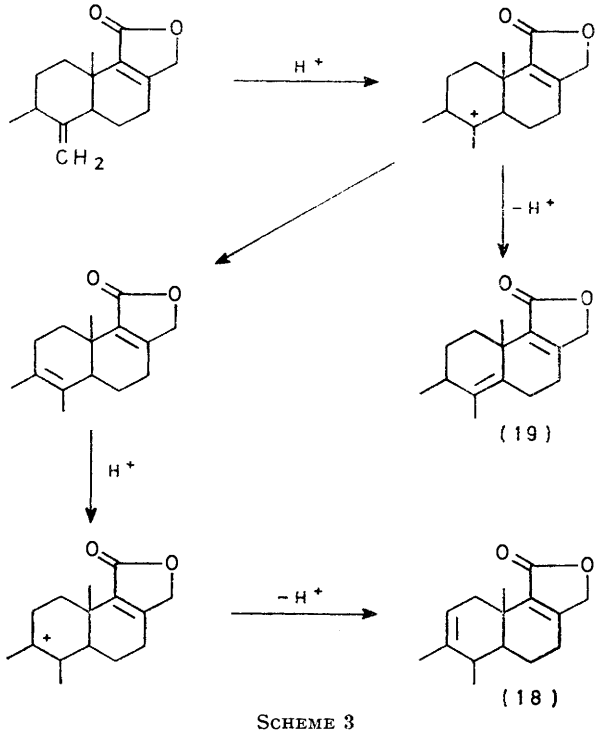
[13] (*a*) R. F. Zurcher, *Helv. Chim. Acta*, 1963, **46**, 2054; (*b*) J. E. Bridgeman, P. C. Cherry, A. S. Clegg, J. M. Evans, Sir Ewart R. H. Jones, A. Kasal, V. Kumar, G. D. Deakins, Y. Monsawa, E. E. Richards, and P. D. Woodgate, *J. Chem. Soc.* (*C*), 1970, 250.

substantial downfield shift. A similar shift is observed when the ketone (12) is converted into the epimers (16) and (17), and this provides conclusive evidence that both these ketones have a *cis*-AB ring junction. As no evidence for a second ketone with a *trans*-AB ring junction could be found in the various epimerization reactions, the C-3 secondary methyl group in (12) and hence that in (1) is assigned the equatorial, 3β-configuration, and the relatively small change in the chemical shift of this methyl group when the n.m.r. spectrum is measured in $CDCl_3$ and in benzene [$\delta(CDCl_3) - \delta(C_6H_6) = 0.05$] is consistent with this structural assignment.[8] With the configuration of the methyl group at C-3 determined the complete stereochemistry of colorata-4(13),8-dienolide is established as represented in structure (1).

C.d. data permit a structural distinction between the oxo-compounds (16) ($\Delta\varepsilon$ + 1.80) and (17) ($\Delta\varepsilon$ + 0.52). *cis*-4-Oxo-decalins and steroids with a 5β-H exhibit a positive Cotton effect.[14] The axial epimer (16) would be predicted to have the larger molecular ellipticity and the $\Delta\varepsilon$ difference (−1.28) between (16) and (17) is reasonable for a methyl group at C-3. It is perhaps surprising that the axial epimer should be the major. The slightly lower value of the chemical shift of the 10β-methyl group in (16) than in (17) (Table 3) indicates a slight flattening of ring A in (16) and the attendant increase in stability may be a factor in determining the ratio of epimers. The n.m.r. and c.d. data are consistent with structures (16) and (17).

The positive Cotton effect ($\Delta\varepsilon$ + 0.47) exhibited by the AB-*trans*-ketone (12) is more difficult to account for. A negative Cotton effect of considerable amplitude would be predicted for this ketone irrespective of whether the C-3 methyl group is axial or equatorial.[14] The major complication is the presence of the αβ-unsaturated lactone system and its possible effect on the ketone c.d. The double bond is γ with respect to the oxo-group and from models there does not appear to be any possibility of orbital overlap. The zig-zag coplanar arrangement of the bonds linking the lactone carbonyl group with the C-4 oxo-group is favourable for 'through-bond' interaction. When an electron withdrawing (−*I*) group [for example the 8-enolide system in (12)] is linked in this way to a carbonyl group the value of $\Delta\varepsilon$ is reduced ('dissignate effect' or 'anti-octant behaviour') and could possibly, in an extreme case, be reversed.[15] 6-Methylene-5α-cholestan-3-one shows a reduced c.d. and 5α-cholest-6-ene-3-one a sign reversal, each due to electron withdrawal through the σ-framework, although some 'back-donation' from the 6-methylene π-orbital through favourably aligned orbitals lessens the observed effect in this compound.[16] Models indicate that while the relative orientations of the C=O and C=C bonds in the 6-methylene compound and the pattern of the intervening C–C bonds resemble those in structure (12), the latter lacks the overlap possibilities needed for effective back-donation. A fairly strong 'anti-octant' ('dissignate') effect should therefore come from the 8,9-double bond in (12) and electron withdrawal due to the lactone carbonyl should enhance this effect.[15c]

Colorat-8-enolide (5) was unchanged after attempted isomerization under both basic and acidic conditions. Colorata-4(13),8-dienolide (1) was resistant to basic isomerization, but with formic acid in chloroform gave the isomers (18) and (19) in the ratio 7 : 3. Both



SCHEME 3

compounds (18) and (19) contain vinylic methyl groups [(18) δ 1.66, 1.67, 1.68, 1.69 (q); (19) δ 1.67]. In the n.m.r. spectrum of (19) the 10β-methyl signal appears at δ 1.29, which is the value predicted from substituent effect data for the proposed structure, with colorat-8-enolide (5) as the parent compound [1.10 − 0.06 (4β-Me) + 0.250 (4-Me-4,5-ene) = 1.290].

The double bond in structure (18) must be in the 2,3-position and the only question that arises is the configuration of the AB ring junction. The conversion of 5α,14α-androstane into 5β,14α-androstane (AB-*cis*) is accompanied by a downfield shift of 0.13 p.p.m. of the signal from the 10β-methyl group. The 10β-methyl signal of (18) is 0.08 Hz upfield from the 10β-methyl signal of (5). Clearly compound (18) does not have a *cis*-configuration for the AB ring junction since whether in the steroidal or non-steroidal conformation a pronounced downfield shift of the 10β-methyl signal would be predicted. Homoallylic coupling of the 3-methyl group with the α-proton at C-1 and allylic coupling with the proton at C-2 would be

[14] D. N. Kirk, W. Klyne, and S. R. Wallis, *J. Amer. Chem. Soc.*, 1961, **83**, 350; W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *ibid.*, p. 4013.

[15] (*a*) G. P. Powell and J. Hudec, *Chem. Comm.*, 1961, 806; (*b*) D. N. Kirk and W. Klyne, *J.C.S. Perkin I*, 1974, 1076; (*c*) personal discussion with Dr D. N. Kirk.

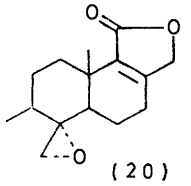
[16] G. P. Powell, R. N. Totty, and J. Hudec, *J.C.S. Perkin I*, 1975. 1015.

expected and the quartet of closely spaced lines observed for the vinylic methyl signal is predictable for structure (18). The formation of compounds (18) and (19) is depicted in Scheme 3. The methyl group at C-4 in (18) is β as a result of preferred α-face attack on the postulated $\Delta^{3(4)}$-intermediate or because of equilibration under the conditions (98% formic acid) employed.

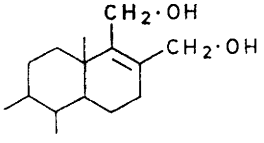
Oxidation of compound (5) with chromium trioxide in 95% acetic acid gave, in addition to the oxo-compound (6), the alcohols (7) and (8). When the oxidant was Beckmann's mixture in acetic acid, sodium dichromate–sulphuric acid, or chromium trioxide in 98% acetic acid the only product was the ketone (6). The 10β-methyl resonances for (7) (δ 1.21) and (8) (δ 1.08) permit the identification of (7) as the 7β- and (8) as the 7α-hydroxy-epimer. The considerable downfield shift in the 10β-methyl signal of (7) caused by the introduction of a 7β-hydroxy-group (0.11 p.p.m.) indicates a flattened chair conformation for ring B.

Treatment of compound (1) with *m*-chloroperbenzoic acid gave the epoxide (20) in quantitative yield. The n.m.r. spectrum [two one-proton doublets, δ 2.54 and 2.58, and 2.77 and 2.81 (AB pattern, CH_2 of oxiran)] is consistent with the proposed structure.

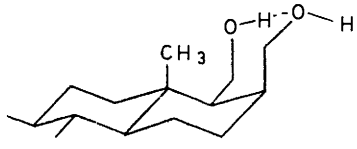
Reduction of colorat-8-enolide (5) with lithium aluminium hydride produced three diols (21)—(23) in the ratios



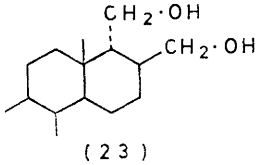
(20)



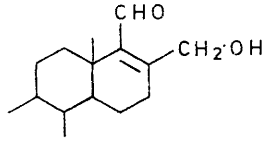
(21)



(22)



(23)



(24)

15 : 3 : 4. These could only be separated by multiple preparative layer chromotagraphy (× 9). The n.m.r. absorption [δ 4.03 and 4.05, and 4.11 and 4.14, two doublets, HO·CH_2–C=C–CH_2·OH] of the major product (21) identified it as the 8,9-enediol. Both (22) and (23) are saturated. The 10β-methyl signal for (22) appears at δ 1.01 and that for (23) at δ 0.77. A hydroxymethyl group does not significantly affect the chemical shift of a 1,3-diaxial methyl group [*cf.* the C-10 methyl signals from (5) and (11)]. The signal at δ 0.77 is close to that to be expected from a 10β-methyl group in a *trans*-decalin. By comparison the 10β-methyl group of (22) (δ 1.01) is deshielded by 0.24 p.p.m. This deshielding is similar to that produced by a hydroxy-group in a 1,3-diaxial relationship. An oxygen function must be fixed in a 1,3-diaxial relationship to the 10β-methyl group and the hydrogen bonded hydroxy-group of structure (22) will meet this requirement. The i.r. spectrum of (22) in CCl_4 (0.005M) shows strong intramolecular hydrogen bonding (3 530 and 3 625 cm^{-1})[17] and requires a *cis*-relationship for the two hydroxymethyl groups. An 8β,9β-configuration for the two hydroxymethyl groups will account uniquely for the n.m.r. and i.r. data. On the other hand the i.r. spectrum of (23) under similar conditions contains two strong sharp singlets at 3 600 and 3 630 cm^{-1}. The absence of any absorption arising from intramolecular hydrogen bonding requires that both the hydroxymethyl groups in (23) should be axial and hence 8β,9α. The reduction must proceed through the intermediate (24), which by direct reduction of the aldehyde group will give (21). The reduction of the conjugated double bond as well as the carbonyl group in αβ-unsaturated carbonyl compounds with lithium aluminium hydride is not uncommon.[18]

The new lactone (1) is a rearranged bicyclofarnesane and presumably owes its biogenesis to a cation-induced migration of a methyl group from C-4 to C-3 followed by loss of a proton from C-13.

EXPERIMENTAL

Experimental procedures *etc.* are as described in Part VI.[19] N.m.r. data included in Tables are not repeated in the Experimental section. Analyses were performed by the microanalytical laboratory of this department under the direction of Professer A. D. Campbell.

Extraction.—In a typical extraction, the air-dried bark of *Pseudowintera colorata* (2.03 kg) was ground to a fine powder in a Wiley mill and extracted (Soxhlet) with hexane (4 l) for 40 h. After removal of acidic (Na_2CO_3) and phenolic (NaOH) material from the concentrated extract the solvent was removed and the neutral fraction (43.2 g) chromatographed in hexane on alumina (1 270 g). The E–H (3 : 7) eluate (8.62 g) was purified by multiple (× 5) p.l.c. on silica gel with E–H (3 : 2) and after crystallization from 95% ethanol gave *colorata*-4(13),8-*dienolide* (1) (4.02 g), m.p. 132—133° (sublimed sample); $[\alpha]_D^{20}$ +292.1° (*c* 0.47 in $CHCl_3$); $\nu_{max.}$ 1 730, 1 655 (–C=C–CO–O–), 1 640 and 885 (C=CH_2), and 780 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 751 and 1 662 (C=C–CO–O) and 1 635 cm^{-1} (C=CH_2); δ 4.62 and 4.82 (2 H, d, C=CH_2) and 4.82 (2 H, s, CH_2 of butenolide); δ (C_6D_6) 3.86 and 3.88 (2 H, d, CH_2 of butenolide), and 4.57 and 4.80 (2 H, d, C=CH_2); *m/e* 232 (M^+), 217, 91, and 77 (100%) (Found: C, 77.5; H, 8.7. $C_{15}H_{20}O_2$ requires C, 77.5; H, 8.7%).

Colorat-8-*enolide* (5).—Colorata-4(13),8-dienolide (1) (50 mg) in ethanol (10 ml) was hydrogenated over pre-reduced Adams catalyst (20 mg) for 20 min. Removal of catalyst and solvent left *colorat*-8-*enolide* (5) (50 mg), m.p. 93—94°

[17] L. P. Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.
[18] F. A. Hochstein and W. J. Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3484.
[19] R. E. Corbett and R. A. J. Smith, *J. Chem. Soc.* (*C*), 1969, 44.

(sublimed sample); $\nu_{max.}$ 1 728 and 1 653 (–C=C–CO–O–) and 781 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 762 and 1 668 cm^{-1} (C=C–CO–O); δ 4.54 (2 H, s, CH_2 of butenolide); δ (C_6D_6) 3.74br (2 H, s, CH_2 of butenolide); *m/e* 234 (M^+), 219, 123 (100%), 91, 59, 55, and 41 (Found: C, 77.3; H, 9.6. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.4%).

7-*Oxocolorat*-8-*enolide* (6).—(*a*) A solution of colorat-8-enolide (5) (110 mg) in acetic acid (4 ml) and Beckmann's mixture, prepared by mixing potassium dichromate (6.0 g, 1 mol. equiv.) with concentrated sulphuric acid (8.0 g, 4 mol. equiv.) and water (27 g) (1 ml), was kept at room temperature for 24 h. Work-up in the usual way and p.l.c on silica gel with E–H (3 : 2) gave unchanged (5) (52.5 mg) and 7-*oxocolorat*-8-*enolide* (6) (20.5 mg), m.p. 75.5—77° (sublimed sample); $\nu_{max.}$ 1 724 (butenolide), 1 691 (αβ-unsaturated cyclohexenone), and 782 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 775 (butenolide) and 1 697 cm^{-1} (αβ-unsaturated cyclohexenone); δ 2.82 (2 H, q, CH_2·CO) and 4.82 (2 H, s, CH_2 of butenolide) (Found: C, 72.7; H, 8.3. $C_{15}H_{20}O_3$ requires C, 72.5; H, 8.1%).

(*b*) Oxidation of compound (5) (50 mg) in acetic acid (2 ml) with sodium dichromate (1.56 g) in a mixture of concentrated sulphuric acid (1.1 ml) and water (8.9 ml) at room temperature for 22 h gave, after work-up and purification by p.l.c. on silica gel with E–H (7 : 3), unchanged (5) (32 mg) and (6) (6.5 mg).

(*c*) Compound (5) (256 mg) in CrO_3–98% acetic acid (130 mg in 6 ml) was kept at 40 °C and additional CrO_3–98% acetic acid (2 ml each) was added at intervals of 2 h. After 8 h the reaction was worked up in the usual way and gave unchanged (5) (100 mg) and (6) (42 mg).

(*d*) Compound (5) (971 mg) in acetic acid (25 ml) containing CrO_3 (537 mg) was stirred at room temperature for 48 h. Work-up in the usual way, followed by p.l.c. on silica gel with E–H (7 : 3), gave, in order of decreasing R_F values, unchanged (5) (378 mg), (6) (149 mg), (7) (20 mg), and (8) (18 mg). 7β-*Hydroxycolorat*-8-*enolide* (7) had m.p. 133—134° (sublimed sample); $\nu_{max.}$ 3 470 (OH), 1 740, 1 675 (butenolide), and 783 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 3 630 and 3 600 (non-bonded OH), 3 500 (bonded OH), 1 750 and 1 720, and 1 690 (butenolide) cm^{-1}; δ 3.65 (1 H, m, $W_{\frac{1}{2}}$ 16 Hz, CH·OH) and 4.84 (2 H, s, CH_2 of butenolide) (Found: C, 71.6; H, 8.6. $C_{15}H_{22}O_3$ requires C, 72.0; H, 8.9%).

7α-*Hydroxycolorat*-8-*enolide* (8) had m.p. 104—105° (sublimed sample); $\nu_{max.}$ 3 450 (OH), 1 735, 1 661 (butenolide), and 783 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 3 625 and 3 600 (non-bonded OH), 3 500 (bonded OH), 1 758, and 1 671 cm^{-1} (butenolide); δ 3.65 (1 H, m, $W_{\frac{1}{2}}$ 16 Hz, C*H*·OH) and 4.57 (2 H, s, CH_2 of butenolide) (Found: C, 72.0; H, 8.9. $C_{15}H_{22}O_3$ requires C, 72.0; H, 8.9%).

7-*Oxocolorata*-5,8-*dienolide* (9).—7-Oxocolorat-8-enolide (6) (50 mg) in glacial acetic acid (5 ml) was heated under reflux with selenium dioxide (150 mg) for 2 h. The solid residue was filtered off and the filtrate was worked-up in the usual way to give a yellow oil (48 mg). P.l.c. on silica gel with E–H (7 : 3) gave 7-*oxocolorata*-5,8-*dienolide* (9) (33.5 mg), m.p. 122—124° (sublimed sample); $\nu_{max.}$ 1 760 (butenolide), 1 682, 1 646 (cyclohexadienone), and 782 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 772 (butenolide), 1 685, and 1 654 cm^{-1} (cyclohexadienone); δ 4.99 (2 H, s, CH_2 of butenolide) and 6.24 (1 H, s, C=C*H*–CO) (Found: C, 73.4; H, 7.7. $C_{15}H_{18}O_3$ requires C, 73.1; H, 7.3%).

7-*Oxocoloratanolide* (10).—7-Oxocolorat-8-enolide (6) (30 mg) in glacial acetic acid (5 ml) was heated under reflux with zinc dust (1.3 g) for 3.5 h. Removal of the zinc dust by filtration and work-up of the filtrate in the usual way followed by p.l.c. on silica gel with E—H (7 : 3) gave 7-*oxocoloratanolide* (10) (30 mg) (sublimed sample); $\nu_{max.}$ 1 770 (butanolide) and 1 698 cm^{-1} (cyclohexanone); $\nu_{max.}$ (CCl_4) 1 780 (butanolide) and 1 710 cm^{-1} (cyclohexanone); δ 2.83 (1 H, t, *J* 11 Hz, CH–C=O), 3.32 (2 H, CH_2–C=O), 4.41 (2 H, d, *J* 4.5 Hz, CH_2 of butanolide) (Found: C, 72.0; H, 9.2. $C_{15}H_{22}O_3$ requires C, 72.0; H, 8.9%).

4α,13-*Dihydroxycolorat*-8-*enolide* (11).—Colorata-4(13),8-dienolide (1) (56 mg) in dry pyridine (15 ml) was stirred with osmium tetraoxide (428 mg) at room temperature. After 1 h, water (30 ml), pyridine (20 ml), and sodium disulphite (1.84 g) were added and the mixture was stirred for a further 30 min. Work-up involved dilution, extraction with chloroform, and washing with saturated aqueous citric acid and gave a colourless gum (73.5 mg). P.l.c. on silica gel with ether gave the *diol* (11), which after distillation (125° at 0.01 mmHg) had $\nu_{max.}$ (film) 3 360 (OH), 1 730, 1 665 (butenolide), and 782 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 3 620, 3 520 (OH), 1 750, and 1 658 cm^{-1} (butenolide); δ 3.65 (2 H, q, CH_2·OH) and 4.59 (2 H, s, CH_2 of butenolide) (Found: C, 67.5; H, 8.5. $C_{15}H_{22}O_4$ requires C, 67.6; H, 8.3%).

13-*Nor*-4-*oxocolorat*-8-*enolide* (12).—The diol (11) (80.5 mg) in dry benzene (40 ml) was stirred at room temperature with acetic acid-free lead tetra-acetate (200 mg). After 2 h ethylene glycol (5 drops) was added and the reaction worked up in the usual way. P.l.c. of the product (60 mg) on silica gel with ether gave 13-*nor*-4-*oxocolorat*-8-*enolide* (12), m.p. 208.5—209.5° (sublimed sample); $\lambda_{max.}$ 219 nm (9 036); $\nu_{max.}$ 1 734, 1 664 (butenolide), 1 704 (cyclohexanone), and 782 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 750, 1 660 (butenolide), and 1 708 cm^{-1} (cyclohexanone); δ 4.63 (2 H, s, CH_2 of butenolide) (Found: C, 71.8; H, 7.8. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7%).

4β-*Hydroxy*-13-*norcolorat*-8-*enolide* (13).—13-Nor-4-oxocolorat-8-enolide (12) (50 mg) in dioxan–methanol–water (20 ml) (5 : 5 : 1 v/v) was heated under reflux with sodium borohydride (50 mg). After 4 h 2M-hydrochloric acid (5 drops) was added and the mixture heated under reflux for a further 1 h. Work-up, followed by p.l.c. on silica gel with ether, gave the 4β-*ol* (13) (50 mg), m.p. 180—181° (sublimed sample); $\lambda_{max.}$ 220 nm (9 600); $\nu_{max.}$ 3 427 (OH), 1 720, 1 652 (butenolide), and 784 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 3 638 (OH), 1 750, and 1 652 cm^{-1} (butenolide); δ 3.74 (1 H, m, C*H*·OH) and 4.55 (2 H, s, CH_2 of butenolide). (Found: C, 71.4; H, 8.7. $C_{14}H_{20}O_3$ requires C, 71.2; H, 8.5%).

4-*Acetoxy*-13-*nor*-5β*H*-*colorata*-3,8-*dienolide* (14) *and* 4-*Acetoxy*-13-*norcolorata*-3,8-*dienolide* (15).—13-Nor-4-oxocolorat-8-enolide (12) (53 mg) was dissolved in acetic anhydride (10 ml) containing dehydrated toluene-*p*-sulphonic acid (55 mg) and the solvent was slowly distilled off through an unpacked column during 24 h. Work-up, which included extraction with ether and washing with saturated aqueous sodium hydrogen carbonate followed by p.l.c. on silica gel with benzene–ethyl acetate (4 : 1), gave a colourless oil (51.5 mg), which was separated by multiple p.l.c. (× 4) on silica gel with E–H (1 : 1) into compounds (14) (42 mg) (higher R_F) and (15) (9 mg). The 5β*H*-*dienolide* (14) had m.p. 104—108° (sublimed sample); $\nu_{max.}$ 1 740, 1 670 (butenolide and αβ-unsaturated acetate), and 782 cm^{-1} (C=C); δ 2.15 (3 H, s, OAc) and 4.63 (2 H, s, CH_2 of butenolide); *m/e* 276 (M^+) and 69 (100%). (Found: C, 69.5; H, 7.6. $C_{16}H_{20}O_4$ requires C, 69.5; H, 7.3%). The *dienolide* (15) after distillation (80° at 0.001 mmHg) had $\nu_{max.}$ 1 745, 1 660 (butenolide and αβ-unsaturated acetate), and 782

cm^{-1} (C=C); δ 2.16 (3 H, s, OAc) and 4.59 (2 H, s, CH_2 of butenolide) (Found: C, 69.4; H, 7.3%).

5βH-4-Oxo-13-norcolorat-8-enolide (16) *and its 3βH-Epimer* (17).—4-Oxo-13-norcolorat-8-enolide (12) (50 mg) in ethanol (4 ml) was heated under reflux with 0.5M-potassium hydroxide (1.5 ml) for 3 h. Work-up in the usual way gave a colourless liquid (50 mg) which after multiple (× 3) p.l.c. on silica gel with E–H (3 : 2) gave the ketones (16) (30 mg) [same R_F as the parent ketone (12)] and (at higher R_F) (17) (19 mg). The *ketone* (16) had m.p. 141° (sublimed sample); $\nu_{max.}$ 1 730, 1 670 (butenolide), 1 705 (cyclohexanone), and 780 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 750, 1 670 (butenolide), and 1 705 cm^{-1} (cyclohexanone); δ 4.65 (2 H, s, CH_2 of butenolide) (Found: C, 72.0; H, 7.9. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7%). The *ketone* (17) had m.p. 136.5—137.5° (sublimed sample); $\nu_{max.}$ 1 740, 1 667 (butenolide), 1 695 (cyclohexanone), and 782 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 750, 1 670 (butenolide), and 1 710 cm^{-1} (cyclohexanone); δ 4.55 (2 H, s, CH_2 of butenolide) (Found: C, 72.0; H, 8.0%).

Isomerization of the Ketone (16).—The ketone (16) (5 mg) in ethanol (5 ml) was heated under reflux with 0.5M-potassium hydroxide (1 ml) for 3 h. Multiple p.l.c. (× 2) with E–H (3 : 2) gave the ketones (16) and (17) in the ratio 3 : 2.

Hydrolysis of the Enol Acetate (14).—The enol acetate (14) (60 mg) in 95% ethanol (10 ml) was heated under reflux with 2M-sulphuric acid (0.5 ml) for 9 h. Work-up in the usual way followed by multiple p.l.c. (× 3) on silica gel with E–H (4 : 1) gave, in order of decreasing R_F values, the ketone (17) (14 mg), the enol acetate (14) (24 mg), and the ketone (16) (22 mg). The spectral characteristics, (i.r. and n.m.r.) of the three products were identical with those of authentic specimens.

Colorata-2,8-dienolide (18) *and Colorata-4,8-dienolide* (19).—Colorata-4(13),8-dienolide (1) (514 mg) in chloroform (20 ml) containing 98—100% formic acid (20 ml) was heated under reflux for 19 h. Work-up, including washing with aqueous sodium hydrogen carbonate (saturated), and multiple (× 15) p.l.c. on silica gel with E–H (3 : 17), gave compounds (18) (350 mg) and (19) (154 mg). *Colorata-2,8-dienolide* (18) had m.p. 101.5—102.5° (sublimed sample); $\nu_{max.}$ 1 740, 1 670 (butenolide), and 782 cm^{-1} (C=C); δ 2.34 (2 H, q, CH_2–C=C), 4.58 (2 H, s, CH_2 of butenolide), and 5.36 (1 H, m, C=CH) (Found: C, 77.4; H, 8.9. $C_{15}H_{20}O_2$ requires C, 77.5; H, 8.7%). *Colorata-4,8-dienolide* (19) had m.p. 122—123° (sublimed sample); $\nu_{max.}$ 1 740, 1 662 (butenolide), and 782 cm^{-1} (C=C); δ 4.58 (2 H, s, CH_2 of butenolide) (Found: C, 77.9; H, 8.9%).

4α,13-Epoxycolorat-8-enolide (20).—*m*-Chloroperbenzoic acid (520 mg) was added to a solution of colorata-4(13),8-dienolide (1) (500 mg) in chloroform (20 ml) and the mixture was kept at room temperature for 24 h. Work-up followed by p.l.c. on silica gel with benzene–ethyl acetate (9 : 1) gave the *epoxide* (20) (480 mg), m.p. 118—119° (sublimed sample); $\lambda_{max.}$ 219 nm (ε 11 646); $\nu_{max.}$ 1 727, 1 665 (butenolide), and 782 cm^{-1} (C=C); $\nu_{max.}$ (CCl_4) 1 766 and 1 670 cm^{-1} (butenolide); δ 2.68 (2 H, ABq, $W_{\frac{1}{2}}$ 16 Hz, oxiran CH_2) and 4.61 (2 H, s, CH_2 of butenolide) (Found: C, 72.6; H, 8.1. $C_{15}H_{20}O_3$ requires C, 72.5; H, 8.1%).

Reduction of Colorat-8-enolide (5) *with Lithium Aluminium Hydride*.—The lactone (5) (220 mg) in dry ether (40 ml) was stirred with the hydride (296 mg) at room temperature for 15 min. Work-up followed by multiple (× 9) p.l.c. on silica gel with E–H (1 : 1) gave, in order of decreasing R_F values, the diols (23) (28.5 mg), (22) (22.5 mg), and (21) (108.5 mg). *3,4,4a,5,6,7,8,8a-Octahydro-5,6,8a-trimethylnaphthalene-1,2-diyldimethanol* (21), after distillation (75° at 0.02 mmHg), had $\nu_{max.}$ 3 330 cm^{-1} (OH); $\nu_{max.}$ (CCl_4) 3 625 (non-bonded OH) and 3 520 cm^{-1} (bonded OH); δ 4.03 and 4.05, and 4.11 and 4.14 each [2 H, d, CH_2(OH)–C=C–CH_2-(OH)] (Found: C, 75.8; H, 11.1. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%). *Decahydro-5,6,8a-trimethylnaphthalene-cis-1,2-diyldimethanol* (22) had m.p. 111—112° (sublimed sample); $\nu_{max.}$ 3 250 cm^{-1} (OH); $\nu_{max.}$ (CCl_4) 3 630 (non-bonded OH) and 3 500 cm^{-1} (bonded OH); δ 3.555 (2 H, d, *J* 0.035 Hz, CH_2·OH) and 3.81 (2 H, m, $W_{\frac{1}{2}}$ 16 Hz, CH_2·OH) (Found: C, 75.1; H, 11.6. $C_{15}H_{28}O_2$ requires C, 75.0; H, 11.7%). The trans-*diol* (23), after distillation (78° at 0.02 mmHg), had $\nu_{max.}$ 3 320 cm^{-1} (OH); δ 3.52 (2 H, q, $W_{\frac{1}{2}}$ 12 Hz, CH_2·OH) and 3.84 (2 H, m, $W_{\frac{1}{2}}$ 16 Hz, CH_2·OH) (Found: C, 74.6; H, 11.3%).

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