

The Chemistry of the Order Araucariales

3.* Structure and Configuration of Araucarolone and Some Related Compounds from *Agathis australis***

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Araucarolone and three closely related diterpene ketols isolated from *Agathis australis* (Lamb. ex. D. Don) Steud. (= *A. australis* Salisbury) possess structures 1, 2, 32, and 34. Ozonolysis of araucarolone diacetate (4) proceeds anomalously and a more detailed study has therefore been made of ozonolysis and perphthalic acid oxidation of the C-7:C-8 double bond in two isopimarane derivatives (1, 19). The optical rotatory dispersion curves of some 2- and 3-oxo derivatives are discussed.

The natural starting point for chemical investigation of the New Zealand Kauri (*Agathis australis*) is the "fossil" bled resin which has in the past been of considerable economic importance and is readily obtainable. Agathic acid was isolated from the bled resin by Tschirch and Niederstadt¹ in 1901, the presence of *d*- α -pinene and dipentene was demonstrated by Hosking² nearly thirty years later and very recently Gough³ has obtained small amounts of sandaracopimaric and abietic acids. A large part of the "fossil" resin is apparently polymeric^{3,4} but further investigation in this laboratory has shown that the bled resin exuded from the bark of the kauri tree contains a number of compounds closely related to those already isolated. These constituents and the changes involved in the conversion to the "fossil" resin will be discussed in a forthcoming paper.

The wood resin is quite different from the bled resin and contains as principal constituents the diterpene ketols araucarolone, araucarone, araucarol and araucarenolone.⁵ The present paper describes structural work showing that the two compounds present in largest amount, araucarolone (50 % of

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the neutral resin) and araucarone (15 %), have structures 1 and 2, respectively, and discusses some further investigations on the chemistry of these compounds.

Araucarolone (isopimar-7-ene-2,15-dion-3 β ,16-diol),* C₂₀H₃₀O₄, gave infra-red (ν_{\max}^{KBr} 1064, 1094, 1705, 3465 cm⁻¹), ultraviolet ($\lambda_{\max}^{\text{EtOH}}$ max 280 m μ , ϵ 84) and NMR (Fig. 1) spectra consistent with the presence of one primary and one secondary hydroxyl group both lacking hydrogens on the adjacent carbon atoms, a trisubstituted double bond, a methylene group adjacent to a carbonyl group, and four quaternary methyl groups. The mass spectrum confirmed the molecular weight (m/e 334 M) and the presence of a primary carbinol group (m/e 303, $M - \text{CH}_2\text{OH}$).

Reduction of araucarolone with sodium borohydride or lithium hydridoaluminatate gave as the main product a tetrol (3). Selenium dehydrogenation of this compound furnished 1,7-dimethylphenanthrene (19 % yield) identified by its characteristic ultraviolet absorption and by undepressed mixed melting point of the picrate. This indicated that araucarolone probably had a carbocyclic skeleton.

Araucarolone on treatment with acetic anhydride in pyridine gave a diacetate (4). Ozonolysis of the diacetate in ethyl acetate at -70° followed by reduction with zinc and acetic acid gave an epoxide (5), discussed below,

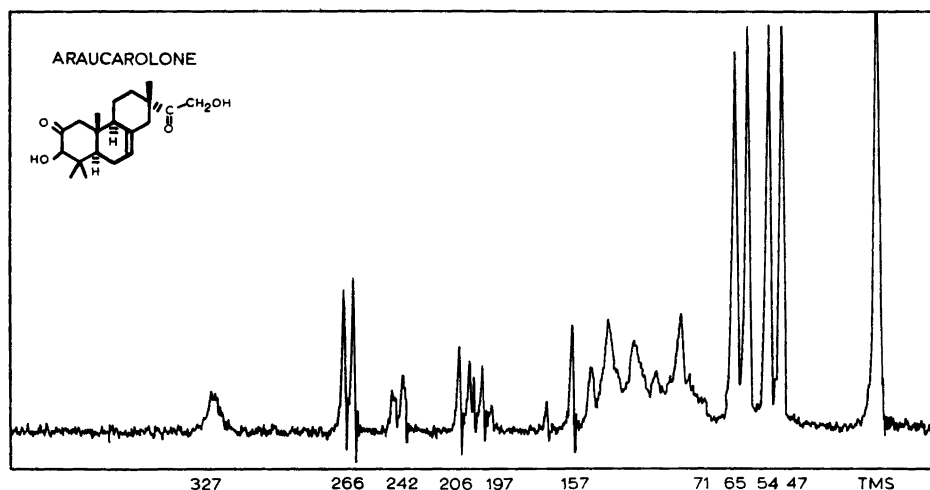
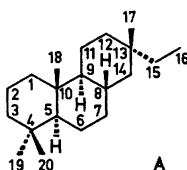
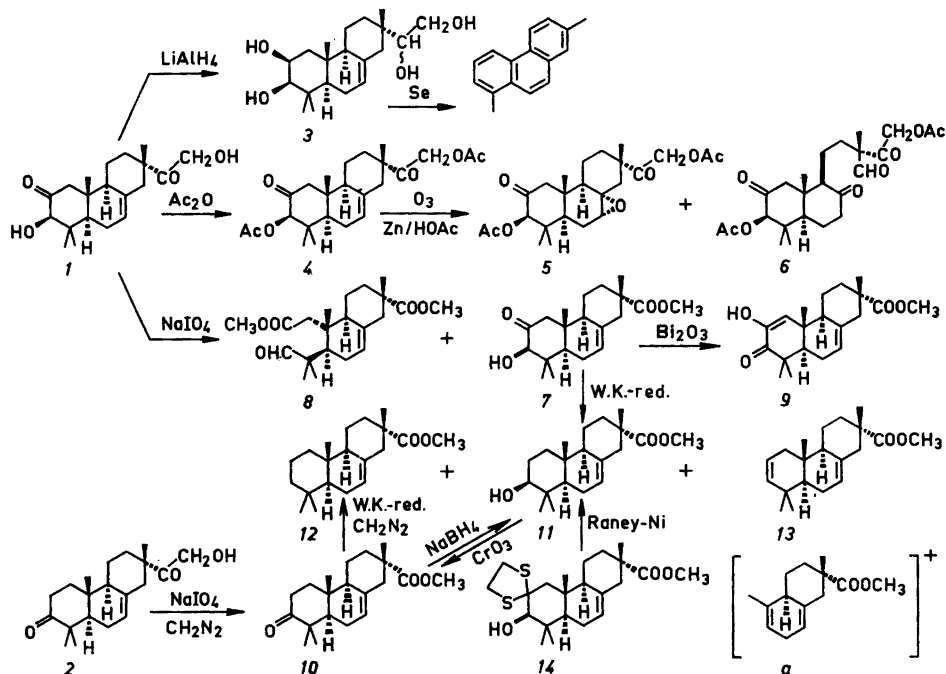


Fig. 1. NMR-spectrum of araucarolone. (Values in cps from TMS at 60 Mc).

* The name isopimarane has been adopted here as a basis for the systematic naming of derivatives of the fully saturated hydrocarbon A.





Scheme 1

and a keto-aldehyde (6). The keto-aldehyde exhibited a sharp singlet at 595 cps due to the presence of a single, tertiary aldehyde group, demonstrating that ozonolysis had produced a cleavage between a tertiary carbon atom and a secondary carbon atom attached to a quaternary carbon atom. For a compound derivable by cyclisation without rearrangement from a geranylgeraniol derivative, this arrangement of eight carbon atoms taken together with the data described above is consistent only with a pimarane skeleton. Further since in the NMR spectrum of araucarolone (Fig. 1) there is no sign of an ethyl group and no splitting of the methylene protons of the primary carbinol group by hydrogen on the adjacent carbon, it followed that the pimarane C-13 ethyl group had to be replaced by a COCH_2OH grouping.

The presence of a COCH_2OH side chain, also supported by the occurrence of a prominent peak at m/e 275 ($M - \text{COCH}_2\text{OH}$) in the mass spectrum of araucarolone, was confirmed by oxidation with periodate followed by esterification with diazomethane to give the methyl ester (7). The simultaneous production in this reaction of a di-ester aldehyde (8) showed that there was a second ketol grouping in araucarolone. In agreement with the NMR spectrum of araucarolone, which shows a methylene group adjacent to the oxo group of the second ketol grouping, bismuth oxide oxidation of the methyl ester 7 gave a diosphenol (9). In a pimarane skeleton this requires the ketol grouping to be in ring A with the carbonyl group at C-2 and the hydroxyl group either at C-1 or at C-3. The two possible ring A diosphenols of dihydromanoyl oxide

can be readily distinguished by infrared and ultraviolet data⁶ but comparison of the corresponding data for the diosphenol 9 did not allow an assignment of its ring A oxygenation pattern.

Araucarone (2), $C_{20}H_{30}O_3$, the second major component obtained from *Agathis australis* wood resin, gave an NMR spectrum (Fig. 2) and a mass spectrum (prominent peaks at m/e 318 (M), 277 ($M-CH_2OH$), and 259 ($M-COCH_2OH$)), which suggest that this compound is similar to araucarolone but lacks the secondary hydroxyl group. The relationship between these two compounds was established chemically by conversion to the same keto-ester (10). This keto-ester was obtained from araucarone by periodate oxidation and methylation and from the ketol ester 7 by Wolff-Kishner reduction, methylation and then chromic acid oxidation of the intermediate hydroxy-ester (11). The hydroxy-ester was also available by sodium borohydride reduction of 10.

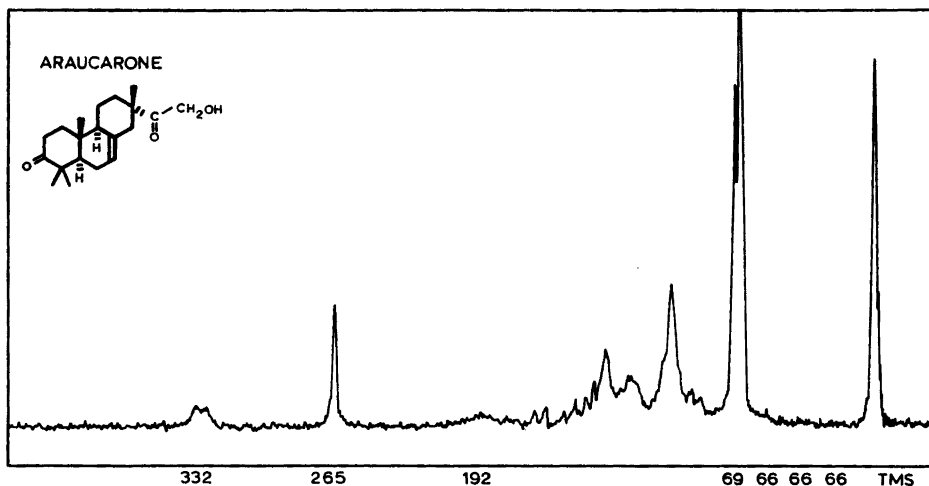
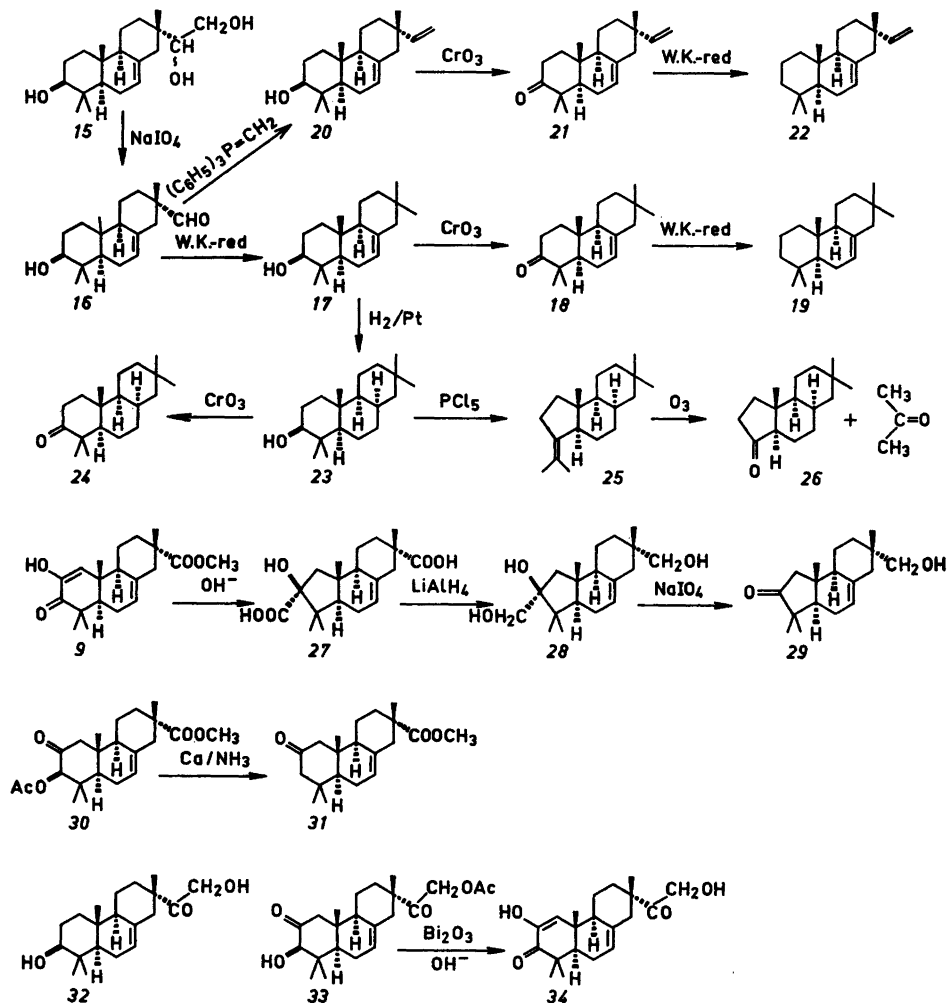


Fig. 2. NMR-spectrum of araucarone. (Values in cps from TMS at 60 Mc).

The main product of the Wolff-Kishner reduction of the ketol ester 7 was not the desired hydroxy-ester 11, but a mixture of compounds with a deoxygenated ring A which could not be separated by thin layer chromatography. It consisted, according to NMR and mass spectra, of the ester 12, also obtained from the keto-ester 10 *via* Wolff-Kishner reduction, and the corresponding Δ^2 -unsaturated compound (13) in a ratio of about 3:1. The mass spectrum of the mixture was nearly identical with that of the ester 12 except for two minor peaks two mass units below the M and $M-15$ peaks of 12 and for two prominent peaks at m/e 220 and 160. These last two peaks are indicative of the presence of a C(2):C(3) double bond, since 13, by analogy with similar compounds,⁷ should readily undergo a retro-Diels-Alder reaction with the formation of ion *a* and the corresponding decarboxylated fragment ($a-60$). Reduc-



Scheme 2

tion of the 2-oxo group of the ketol ester 7 to a methylene group was effected in much better yield by a different route involving acetylation, thioketal formation, saponification and desulfuration of the thioketal 14 with Raney nickel. In addition to the main product (11), the last step also furnished small amounts of the keto-ester 10 and an ester alcohol which is probably the $\Delta^{8(9)}$ isomer of 11. The mechanism involved in Raney nickel reductions of steroidal thioketals has recently been discussed by Djerassi and Williams⁸ (*cf.* also Ref. 9).

The carbon skeleton, the configurations at C-5, C-9, C-10, and C-13, and the position of the double bond in araucarolone (1) and araucarone (2) were established by conversion of the latter to the crystalline 16-norpimar-7-ene (19) and the liquid isopimar-7,15-diene (22) as shown in scheme 2. Reduction with lithium hydrido-aluminate followed by periodate oxidation gave a hydroxy-aldehyde (16). This on Wolff-Kishner reduction, chromic acid oxidation and a second Wolff-Kishner reduction gave 16-norpimar-7-ene, which was shown to be identical with authentic material by mixed melting point, rotation and comparison of infrared and NMR spectra. Conversion of the hydroxy-aldehyde 16 by a Wittig reaction to a diene-alcohol (20) followed by chromic acid oxidation and Wolff-Kishner reduction gave isopimar-7,15-diene, identical with authentic material (NMR, infrared, rotation). The structures of 16-norpimar-7-ene and isopimar-7,15-ene have recently been firmly established^{9,10} and it follows that araucarolone and araucarone have the "normal" configuration shown (1 and 2).

The secondary hydroxyl group of araucarol (32) and the ring A keto group of araucarone have to be at either C-1 or C-3 from the results mentioned. Since the alcohols 11, 17, and 20, from the method of their preparation and their NMR spectra, must have β -oriented hydroxyl groups, the differences in molecular rotation between these compounds and their *p*-nitrobenzoates ($\Delta M = -167^\circ$, -253° , and -244° , respectively) clearly favour the C-3 alternative.¹¹ This was demonstrated chemically by phosphorus pentachloride rearrangement of the saturated alcohol 23 obtained as the main product on catalytic hydrogenation of 17. (The 8α -configuration assigned to 23 follows from the method of preparation and from the positive rotatory dispersion curve of the corresponding ketone 24 (see below).) Ozonolysis of the rearranged product (25) gave acetone, isolated as the 2,4-dinitrophenylhydrazone, and a non-crystalline material exhibiting infrared absorption (1742 cm^{-1}) typical of a five-membered ring ketone (26). These results are compatible only with the presence of a 3β -hydroxyl group in 23; phosphorus pentachloride rearrangement of 1β -hydroxy triterpenes has recently been shown to give A-nor-B-homo derivatives.¹²

Additional proof of the position of the secondary hydroxyl group of araucarolone and the ring A keto group of araucarone was obtained from the rotatory dispersion curves of the ketones 10, 18, and 29 discussed below. The ketone 29 was prepared from the diosphenol 9 by benzilic acid rearrangement to the hydroxy-diacid 27 followed by lithium hydrido-aluminate reduction and periodate oxidation of the resulting triol (28). The configuration of the hydroxy-diacid 27 follows from the stereoselective nature of the benzilic acid contraction of diosphenols.¹³

Comparison of the ultraviolet spectra of the ketol ester 7 and the corresponding keto-ester 31, which was obtained by reduction of the ketol ester acetate 30 with calcium in liquid ammonia, showed that the absorption maximum of 7 occurred at a shorter wavelength ($273\text{ m}\mu$) than that of 31 ($285\text{ m}\mu$), demonstrating that the 3-hydroxyl group in araucarolone (1) is β -oriented. The same result follows from a comparison of the rotatory dispersion curves of 30 and 31. The former curve exhibits the first extremum at slightly shorter wavelength than that of the latter and shows a smaller

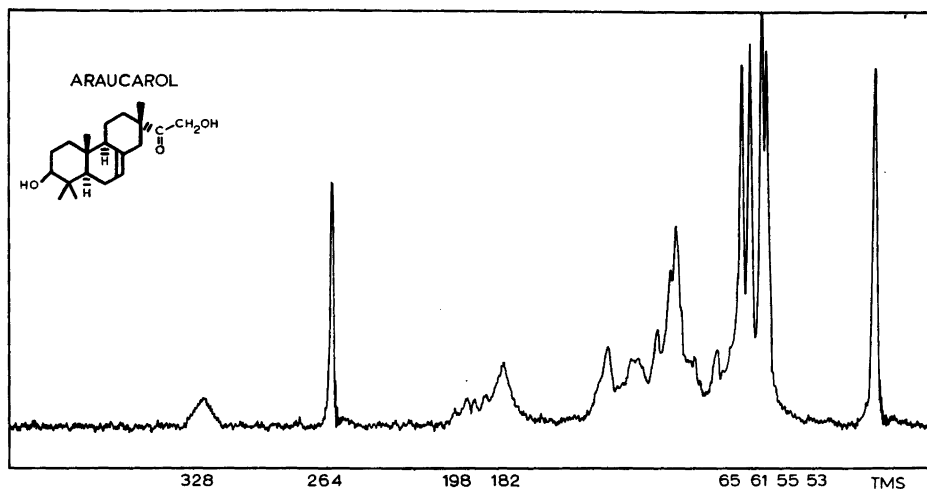


Fig. 3. NMR-spectrum of araucarol. (Values in cps from TMS at 60 Mc).

amplitude. The rotatory dispersion curve of the ketol ester 7 shows only an inflection (*cf.* Table 2).

The evidence described above completely fixes the structures and configurations of araucarolone (1) and araucarone (2). The two minor components from *Agathis australis* wood resin, araucarol (32) and araucarenolone (34), appeared on the basis of spectroscopic data to be closely related to the two main products.

The NMR spectrum of araucarol (Fig. 3) shows bands typical of the ketol side chain and the vinyl proton of the first two compounds (1,2). The quartet

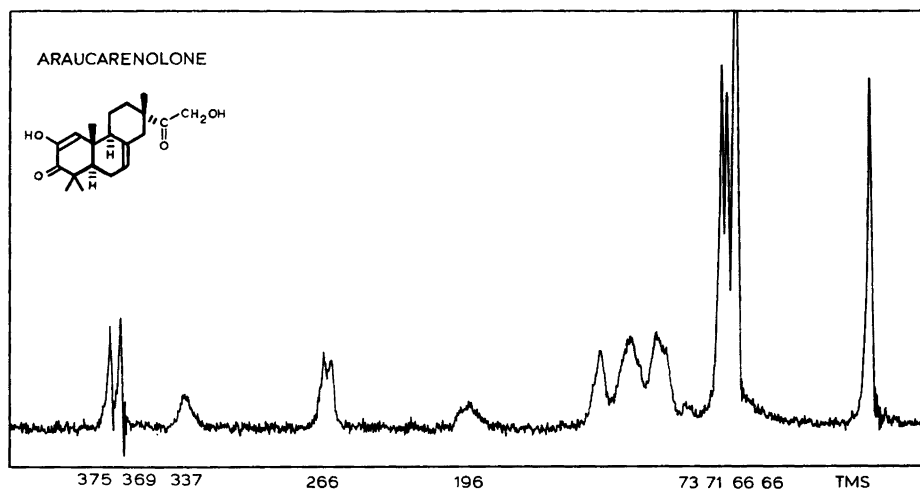


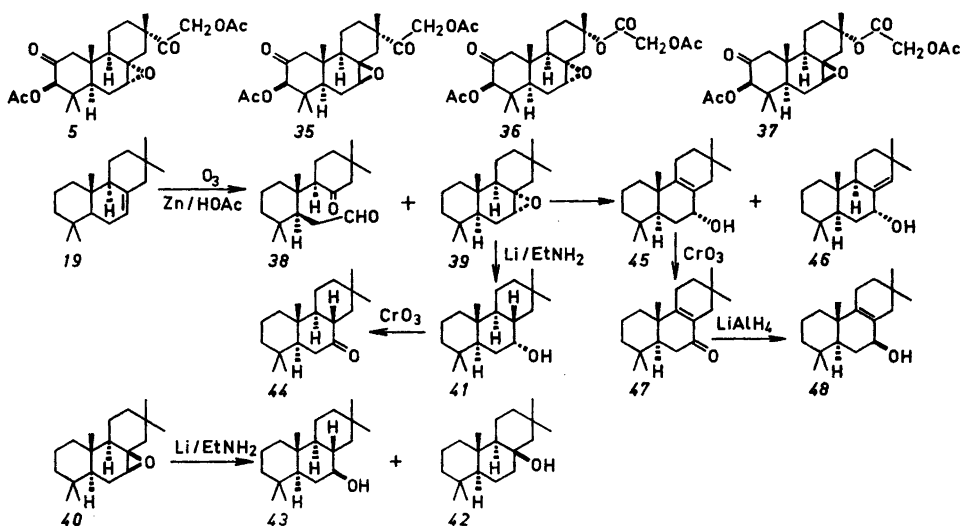
Fig. 4. NMR-spectrum of araucarenolone. (Values in cps from TMS at 60 Mc).

centred at 197 cps suggests the presence of an equatorial hydroxyl group, probably at C-3. Its mass spectrum exhibits prominent peaks at m/e 320 (M), 302 ($M - H_2O$), 279 ($M - CH_2OH$), 271 ($M - H_2O - CH_2OH$), 261 ($M - COCH_2OH$), and 243 ($M - H_2O - COCH_2OH$) supporting these findings. Araucarol on reduction with lithium hydrido-aluminate gave the triol 15 and this on oxidation with periodate followed by esterification with diazomethane gave the hydroxy-ester 11. The identity of these products with those previously obtained from araucarone establishes structure 32 for araucarol.

Araucarenolone (34) gives NMR (Fig. 4), ultraviolet (λ_{\max}^{EtOH} 263 $m\mu$, ϵ 7700) and infrared spectra (ν_{\max}^{Nujol} 1665, 1678 cm^{-1}) which together with the very close similarity of its mass spectrum with that of araucarolone (1) clearly indicate that it is the diosphenol produced by oxidation of araucarolone. It was readily synthesised from araucarolone by brief acetylation to give the 16-mono-acetate (33) followed by bismuth oxide oxidation and mild saponification.

Oxidations with ozone and perphthalic acid

Since the position of the double bond in araucarolone is firmly fixed, it follows that the ozonolysis of araucarolone diacetate (4) is anomalous. To gain further insight into the course of this reaction it was necessary first to establish the structure of the epoxide that is formed as the main product. Similar anomalous cleavage has been observed in the ozonolysis of isopimaric and dihydropimaric acids,¹⁴ but in these reactions nothing is known of the products formed other than those resulting from cleavage at C(8)—C(14).




Scheme 3

To prepare the epoxide in an unequivocal way, araucarolone diacetate (4) was treated with monopero-phthalic acid in ether. This gave a mixture of four epoxides (5, 35, 36, and 37), one of which (5) was shown to be identical with the main ozonolysis product. The four epoxides were separated by chromatography on silica gel and by crystallisation and their structures were elucidated largely from NMR and infrared spectra and analyses (Table 1). They all show an epoxy proton band at about 185 cps but no vinyl proton and no hydroxyl group. The configurations of the epoxide groups in the isomers 5 and 35 were assigned from the epoxy proton band since inspection of Dreiding models indicates that the epoxide proton bond will lie more nearly parallel with the 6α -proton bond in the β -epoxide than in the α -epoxide. Epoxide 35 which shows a doublet (J 4 cps) must therefore be the β -epoxide and epoxide 5 with a slightly broadened singlet at 187 cps must be the α -epoxide. This assignment is supported by the yields of the different products, since the α -epoxide formed by attack on the unhindered side would be expected in the largest yield, and also by comparison with the norpimarane epoxides discussed below.

Epoxides 36 and 37, according to analyses, both contain an oxygen atom additional to the epoxide oxygen. They give NMR spectra essentially similar to those of epoxides 5 and 35 but with considerable displacement of the bands due to the groups around C(13), the methyl group being displaced to lower field and the CH_2OAc band to higher field (see Table 1). Their infrared spectra exhibit bands at higher frequency (1757 cm^{-1}) than those of the simple epoxides 5 and 35 which is indicative of an acetoxy group α to an ester group.¹⁵ These data are consistent with the insertion of an oxygen atom between C(13) and C(15) by a Baeyer-Villiger oxidation of the original epoxides 5 and 35 and this was confirmed by monopero-phthalic acid oxidation of these compounds to give 36 and 37, respectively. The configurations of 36 and 37 at C(13) can be assigned as shown since Baeyer-Villiger oxidations are known to proceed with retention of configuration.¹⁶

Table 1. Epoxides from araucarolone diacetate (NMR values in cps from tetramethylsilane at 60 Mc).

Compound	AcOCH	AcOCH ₂		Methyl protons	Yield %
5 C ₂₄ H ₃₄ O ₇	294	301	187	77 62 53 50	40
35 C ₂₄ H ₃₄ O ₇	297	294	183	83 66 55 53	9
36 C ₂₄ H ₃₄ O ₈	297	274	186	97 65 55 52	19
37 C ₂₄ H ₃₄ O ₈	293	268	184	100 68 54 54	27

In the light of the results from araucarolone diacetate it was of interest to study the action of ozone on the simpler, non-oxygenated analogue, 16-norpimar-7-ene (19), to see if cleavage of the C(8)—C(14) bond was typical Δ^7 -pimarane derivatives. Ozonolysis of 19 gave the epoxide 39 as major product (according to NMR) accompanied by small amounts of the keto-aldehyde 38. The keto-aldehyde was obtained in insufficient amount (5 %)

for complete purification or for characterisation except by its NMR spectrum but its structure is clear from the aldehyde proton triplet at 595 cps (J 1.7 cps).

Monoperphthalic acid oxidation of 19 gave as primary products the two expected epoxides 39 and 40 in about a 3:1 ratio. The epoxide obtained as the main product from both ozonolysis and perphthalic acid oxidation moved more slowly on alumina and silica gel and showed an epoxide proton band (175 cps, J 1.4 cps) considerably narrower than that of the other epoxide (J 6 cps). It follows that the former must be the α -isomer (39) and the faster moving epoxide must be the β -isomer (40). This assignment was confirmed by reduction of the epoxides with lithium in ethylamine; the α -epoxide (39) gave 7 α -hydroxynorpimarane (41) in 95 % yield and the β -epoxide (40) gave 8 β -hydroxy-norpimarane (42) in 85 % yield together with a small amount of 7 β -hydroxynorpimarane (43).

The tertiary alcohol 42, which was recovered unchanged after treatment with chromic acid in acetone, was assigned the configuration depicted since only a β -oriented 8-hydroxyl group would cause the observed displacement of two methyl bands to lower field (68 and 61 cps). The configuration of the 7 α -hydroxynorpimarane indicated by a broad $CHOH$ singlet at 228 cps was established by converting it to the equatorial epimer 43 ($CHOH$ sextet at 193 cps, J 5, 11, 11 cps) by oxidation with Jones reagent, giving the 7-oxo compound (44), and then reduction with lithium hydrido-aluminate. Since Jones reagent is known¹⁷ not to cause racemisation of the adjacent asymmetric centre and the ketone 44 could be recovered unchanged after treatment with ethanolic potassium hydroxide at reflux temperature the alcohols 41 and 43 as well as the ketone 44 can all be assigned the 8 β -configuration shown. The position of the oxo group in 44 was confirmed by the mass spectrum of the ketone after deuterium exchange ($EtOD/D_2O/NaOD$) to give the 6,6,8- d_3 -derivative of expected molecular weight (279). Lithium-ethylamine reduction of the two epoxides 39 and 40 thus gives the axial alcohols almost exclusively in both cases.*

The norpimarane epoxides are reasonably stable under neutral conditions but are very sensitive to traces of acid. On treatment with zinc and acetic acid in working up the ozonolysis product the α -epoxide was largely converted to a mixture of the allyl alcohols 45 and 46. Similarly this epoxide (39) when left adsorbed on silica gel for several hours was converted to the $\Delta^{8:9}$ -7 α -ol (45) and in deuteriochloroform in which traces of acid had probably formed immediately gave the $\Delta^{8:14}$ -7 α -ol (46). The products obtained from the β -epoxide (40) under similar conditions usually gave a hydrocarbon mixture, which from its NMR spectrum appeared to consist predominantly of 16-norpimara-7,9(11)-diene.

The structures of the two allyl alcohols follow from their nmr spectra. Both 45 and 46 show broad $CHOH$ singlets indicating equatorial protons at C(7); a $CHOH$ proton at C(14) should give a relatively sharp singlet. The double

* In view of the present results it is interesting that 3 β -acetoxy-7 α ,8 α -epoxyergost-22-ene on reduction with lithium-ethylamine has been reported¹⁸ to give the 8 α -alcohol and not the axial 7 α -isomer. However, the evidence quoted (resistance of the newly formed hydroxyl group to acetylation under normal conditions) does not seem to exclude the latter alternative (*cf.* Ref. 19).

bond position in the $\Delta^{8:9}$ -7 α -ol (45) follows from the presence of a strong allyl proton band (123 cps) and the absence of any vinyl proton band and in the $\Delta^{8:14}$ -7 α -ol (46) it is shown by the narrow vinyl proton band. The structure of the $\Delta^{8:9}$ -7 α -ol was confirmed by oxidation to the corresponding α,β -unsaturated ketone 47 ($\lambda_{\text{max}}^{\text{EtOH}}$ 247 m μ , ϵ 10 000) and reduction of this ketone with lithium hydrido-aluminate to the epimeric $\Delta^{8:9}$ -7 β -ol (48), formed by attack from the less hindered side. This showed a very broad *CHOH* band at 237 cps.

The sensitivity of the epoxides 39 and 40 and the ease of conversion to allyl alcohols parallels the behaviour of steroid 7,8-epoxides.²⁰ Epoxides of 7,8-unsaturated tetracyclic triterpenes are similarly unstable and since our preliminary communication²¹ the first report on a procedure of preparing the α -epoxide of Δ^7 -lanostenyl acetate in pure form has appeared;²² 7,9(11)-dienes have been frequently encountered in earlier work on peracid oxidation (*cf.* Ref. 22) of this type of compound.

In summary, ozonolysis of pimar-7-ene derivatives can apparently proceed *via* three different routes leading to 7 $\alpha,8\alpha$ -epoxide formation, to anomalous, C(8)—C(14), cleavage, and to normal, C(7)—C(8), cleavage. In the compounds investigated here epoxide formation dominates, while normal cleavage occurs only to a very small extent or not at all. Epoxide formation, which may be regarded as the result of stabilisation of an initial ozone-double bond complex by elimination of molecular oxygen due to steric hindrance, is not uncommon²³ and has been encountered in Δ^7 -steroids; *e.g.*, cholest-7-en-3 β -ol gives the α -epoxide.²⁴ The anomalous cleavage observed in the ozonolyses of araucarolone diacetate, and of isopimaric and dihydroisopimaric acids¹⁴ may represent an alternative way for an ozone-double bond complex to stabilise, *e.g.* by a route reminiscent of that outlined for Feist's acid,²⁵ or it may be due to direct allylic attack at C(14) giving an intermediate which could undergo a rearrangement similar to that involved in the conversion of cyclohexene hydroperoxide to hexandial.⁶²

Optical rotatory dispersion data

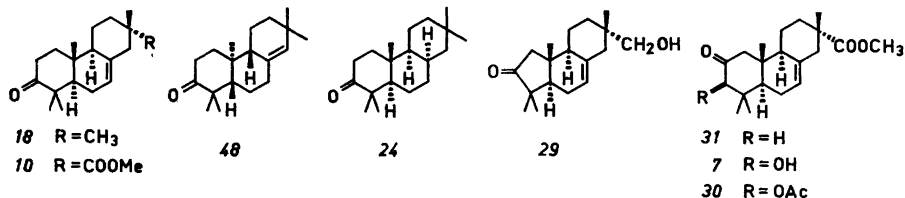
The optical rotatory dispersion curves of several ketones described in the present investigation have been determined through the courtesy of Professor W. Klyne. The results are summarised in Table 2. Previously recorded data for some analogous compounds have been included for comparison.

The 3-oxo compounds 18 and 10 give curves which are similar to 4,4-dimethyl-5 α -cholest-7-en-3-one and 3-oxo- Δ^7 triterpenes such as lanost-7-en-3-one and baurenone, demonstrating that the conformations of rings A and B are the same and that the contribution of the additional rings are of little importance.^{27,32} The data given for 3-oxo- $\Delta^{8:14}$ compounds such as 48²⁷ and 4,4-dimethyl-5 α -cholest-8(14)-en-3-one²⁷ show that Δ^7 - and $\Delta^{8:14}$ -3-oxopimarene derivatives can not be distinguished in a satisfactory manner by means of their rotatory dispersion curves.

The saturated ketone 24, obtained as the main product on hydrogenation of the C(7)—C(8) double bond, shows a positive Cotton effect in analogy with 3-oxo triterpenes possessing a 8 β -methyl group, *e.g.* hydroxydammarone-II.²⁸

Table 2. Optical rotatory dispersion data for some 2- and 3-oxo terpenes and steroids. All measurements are in methanol (for additional data and details see experimental part). Amplitudes [A] are given as the differences between the molecular rotations ($[\Phi]_1 - [\Phi]_2$) recorded at the extrema, divided by 100, (cf. Ref. 27).

Compound	$[\Phi]_1$	λ (m μ)	$[\Phi]_2$	λ (m μ)	[A]	Ref.
18	- 2 310	314	0	274	- 23	Present work
10	- 2 180	314	+ 440	274	- 26	»
4,4-Dimethyl-5 α -cholest-7-en-3-one	- 1 520	315	+ 1 070	275	- 26	27
48	+ 1 230	315	- 3 010	260	+ 42	27
4,4-Dimethyl-5 α -cholest-8(14)-en-3-one	- 1 650	307.5	+ 530	280	- 22	27
24	+ 1 565	303	- 485	265	+ 20	Present work
Hydroxydammarone-II	+ 3 460	307	- 305	273	+ 38	28
29	+ 7 500	314	- 7 480	263	+ 150	Present work
A-nor-3,3-dimethyl-5 α -cholestan-2-one	+ 11 500	320	-10 600	275	+ 221	29
Colens-14-en-2-one	+ 11 310	317.5	-10 120	275	+ 214	30
31	+ 860	309	- 3 030	260	+ 39	Present work
2-Oxomanoyl oxide	+ 3 480	310	- 3 160	280	+ 66	27
5 α -Cholestan-2-one	+ 4 860	310	- 5 230	267.5	+ 101	31
7	- 1 250	274 (inflex.)				Present work
30	+ 810	308	- 855	276	+ 17	»



Scheme 4

The inversion of curves in going from 4,4-dimethylated 3-oxo steroids (-C.E.) to triterpenes possessing a 8β -methyl group (+ C.E.) has recently been explained in terms of conformational distortions of rings A and B due to the interaction of the 8β -methyl group on the 10β -methyl group.³³ Since the 14-methylene group in the ketone 24 should cause a similar distortion, the positive Cotton effect observed for this compound is in agreement with expectations.

The five-membered ring ketone 29 gives a positive, high amplitude curve similar to those of A-nor-3,3-dimethylcholestan-2-one²⁹ and colens-14-en-2-one.³⁰ The introduction of a double bond, as in 29, or of 1:3-interactions, as in colens-14-en-2-one, seem to have little effect as may be expected on the

basis of the strong "first order" effect associated with the cyclopentanone system.³⁴

The 2-oxo compound 31 exhibits a positive Cotton effect as do 5 α -cholestan-2-one³¹ and 2-oxomanoyl oxide.²⁷ Comparison of amplitudes and 1:3-interactions for these compounds shows changes paralleling those of the 3-oxo series (5 α -cholestan-3-one,³² 4,4-dimethyl-5 α -cholest-7-en-3-one, hydroxydammarenone-II). Thus the difference in amplitude between the compounds with no such interaction and compounds with interacting 4 β - and 10 β -methyl groups is positive both in the 3-oxo ($\Delta A \sim +80$) and the 2-oxo ($\Delta A \sim +60$) series. When there is a further interaction on the 10 β -methyl group by a 8 β -methyl group a negative difference is observed for both the 3-oxo ($\Delta A \sim -60$) and the 2-oxo ($\Delta A \sim -30$) compounds. Unfortunately, the 2-oxo compounds available are not ideal and further examples are required to see to what extent such quantitative effects may be associated with conformational deformations of rings A and B.

EXPERIMENTAL

Melting points were determined on a hot stage and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer No. 21 instrument (NaCl prism) and ultraviolet spectra on a Beckman DK 2 recording spectrophotometer. Mass spectra were determined on an instrument³⁵ with an all glass heated inlet system at 150–200° (energy of electrons 70 eV) and NMR spectra (in CDCl₃) on a Varian DP 60 spectrometer at 60 Mc. NMR frequencies are given in cps relative to tetramethylsilane (using either CHCl₃ or a sideband for frequency calibration).

The optical rotatory dispersion curves, kindly determined by Professor W. Klyne, have been measured on a Bellingham & Stanley/Bendix-Ericsson automatic recording polarimeter, "Polarmatic 62". Micro-analyses by Dr. A. D. Campbell, University of Otago, Dunedin.

The naturally occurring compounds (1, 2, 32, and 34). The naturally occurring compounds were obtained as described elsewhere⁵ and purified by chromatography on silica gel and by recrystallisation from ethanol.

Araucarolone (1, isopimar-7-ene-2,15-dion-3 β ,16-ol) had m.p. 159–161°, [α]_D –42° (CHCl₃, *c* 5.4). (Found: C 72.2; H 9.3. C₂₀H₃₀O₄ requires: C 71.8; H 9.0). Mol.wt. 334 (mass spectrum), $\lambda_{\max}^{\text{EtOH}}$ 280 μ (ϵ 84), ν_{\max}^{KBr} 883, 877, 926, 993, 1037, 1064, 1094, 1188, 1216, 1261, 1301, 1372, 1406, 1443, 1473, 1705, 2950, 3465 cm⁻¹.

Araucarone (2, isopimar-7-ene-3,15-dion-16-ol) had m.p. 115–116°, [α]_D –51° (CHCl₃, *c* 2.2). (Found: C 75.4; H 9.7. C₂₀H₃₀O₃ requires: C 75.4; H 9.5). Mol.wt. 318 (mass spectrum), $\lambda_{\max}^{\text{EtOH}}$ 280 μ (ϵ 68), ν_{\max}^{KBr} 758, 843, 997, 1069, 1120, 1160, 1202, 1279 (broad), 1316, 1371, 1390, 1407, 1438, 1455, 1703 (broad) 2940 (broad) 3465 cm⁻¹, $\nu_{\max}^{\text{CCl}_4}$ 3515, 1707 cm⁻¹.

Araucarol (32, isopimar-7-en-15-one-3 β ,16-diol) had m.p. 135–136°, [α]_D –24° (CHCl₃, *c* 1.7). (Found: C 74.6; H 10.2. C₂₀H₃₂O₃ requires: C 75.0; H 10.1). ν_{\max}^{Film} 760, 816, 832, 856, 925, 998, 1057, 1111, 1285, 1375, 1395, 1452, 1469, 1705 (broad), 3450 cm⁻¹.

Araucarenolone (34, isopimar-1,7-diene-3,15-dione-2,16-diol) had m.p. 143–144°, [α]_D –58° (CHCl₃, *c* 2.0). (Found: C 71.9; H 8.6. C₂₀H₂₈O₄ requires: C 72.3; H 8.5). $\lambda_{\max}^{\text{EtOH}}$ 263 μ (ϵ 7700), $\nu_{\max}^{\text{Nujol}}$ 821, 837, 860, 1008, 1065, 1111, 1665, 1678, 1696, 3400, 3465 cm⁻¹.

Isopimar-7-ene-2 β -3 β -15,16-tetrol (3). Araucarolone (1.4 g), dissolved in methanol (10 ml) was added to a solution of sodium borohydride (1.4 g) in methanol (30 ml) and left overnight. Dilution with water (500 ml) followed by extraction with chloroform gave the tetrol (1.4 g), which on recrystallisation from methanol had the m.p. 229–231°

(decomp.), $[\alpha]_D -11^\circ$ ($(\text{CH}_3)_2\text{SO}$, c 1.1). (Found: C 71.4; H 10.5. $\text{C}_{20}\text{H}_{30}\text{O}_4$ requires: C 71.0; H 10.1). $\nu_{\text{max}}^{\text{Nujol}}$ 1023, 1040, 1066, 1090, 3295, 3445 cm^{-1} .

Dehydrogenation of isopimar-7-ene-2 β -3 β -15,16-tetrol (3). The tetrol 3 (300 mg) was heated at 300–320° with selenium (300 mg) for 24 h. The product was extracted with ether, filtered through alumina, distilled at reduced pressure (0.1 mm) and chromatographed on alumina (15 g). Elution with hexane gave 1,7-dimethylphenanthrene (34 mg) identified by its ultraviolet spectrum $\lambda_{\text{max}}^{\text{Hexane}}$ 252 *infl.* ($\log \epsilon$ 4.85), 257 (4.90), 280 (4.28), 288 (4.18), 301 (4.24), 319 (2.60), 327 (2.46), 335 (2.55), 352 (2.22) $\text{m}\mu$ and by conversion to the picrate, m.p. and mixed m.p. 128–129°.

3 β ,16-diacetoxy-isopimar-7-ene-2,15-dione (4). Araucarolone (3.0 g) in pyridine (15 ml) was treated with acetic anhydride (7 ml) at 40° for 40 h. Methanol (20 ml) was added and the product taken to dryness at water pump pressure. The diacetate (3.38 g), on recrystallisation from isopropyl ether had m.p. 119–120°, $[\alpha]_D +28^\circ$ (CHCl_3 , c 2.2). (Found: C 68.9; H 8.5. $\text{C}_{24}\text{H}_{34}\text{O}_6$ requires: C 68.9; H 8.2). $\nu_{\text{max}}^{\text{Nujol}}$ 994, 1013, 1041, 1065, 1095, 1235 (broad), 1289, 1417, 1725, 1745 cm^{-1} , NMR 356 (HC(7), b), 315 (H C(16), s), 322 (HC(3), s), 114 ($(\text{H}_3\text{CCOO})_2$, s) cps.

Ozonolysis of araucarolone diacetate (4). The diacetate 4 (3 g) in ethyl acetate (15 ml) was treated with ozone at -70° until excess ozone was present as indicated by a permanent blue colour. The solution was poured onto a mixture of zinc (2 g) and acetic acid (5 ml) and left over night. The reaction mixture was filtered and diluted with ether and the solution was washed with aqueous sodium hydrogen carbonate and water. The product was chromatographed on silica gel (300 g) using a hexane-ether gradient. The first fraction (1.98 g) was 7 α ,8 α -oxido-araucarolone diacetate (5) giving infrared and NMR spectra identical with those of authentic material obtained by perphthalic acid oxidation of araucarolone diacetate.

The second fraction gave the keto-aldehyde 6 (0.63 g), which on recrystallisation from ethanol had m.p. 174–175°. (Found C 63.8; H 7.9. $\text{C}_{24}\text{H}_{34}\text{O}_8$ requires: C 64.0; H 7.8). $\nu_{\text{max}}^{\text{Nujol}}$ 1237, 1712, 1724, 1747, 2750 cm^{-1} , NMR: 595 (HC(14), s) cps.

Sodium periodate oxidation of araucarolone (1). Araucarolone (6 g) dissolved in methanol (150 ml) was treated at 0° with a solution of sodium periodate (6 g) in water for 30 min. The reaction mixture was diluted with water (1.5 l) and extracted with ether. The residue (6 g) obtained on evaporation of the solvent was esterified with an ethereal solution of diazomethane. The resulting mixture of esters was chromatographed on alumina (activity 2; 200 g). Elution with isopropyl ether gave the seco-aldehyde diester 8 (2.2 g), which on recrystallisation from aqueous methanol had m.p. 62–63°, $[\alpha]_D -40^\circ$ (CHCl_3 , c 2.0). (Found: C 69.0; H 8.9. $\text{C}_{21}\text{H}_{32}\text{O}_5$ requires: C 69.2; H 8.9). $\nu_{\text{max}}^{\text{Nujol}}$ 1720 (broad), 2730 cm^{-1} , NMR: 576 (HC(3), s), 323 (HC(7), b), 221 ($\text{H}_3\text{COC}(15)$, s), 216 ($\text{H}_3\text{COC}(2)$, s) 146 ($\text{H}_2\text{C}(1)$, s) cps. Elution with ether gave the ketol ester 7 (3.4 g), which on recrystallisation from isopropyl ether had m.p. 123–125°, $[\alpha]_D -39^\circ$, (CHCl_3 , c 1.9). (Found: C 71.9; H 9.4. $\text{C}_{20}\text{H}_{30}\text{O}_4$ requires: C 71.8; H 9.0). $\lambda_{\text{max}}^{\text{EtOH}}$ 273 $\text{m}\mu$ (ϵ 49), $\nu_{\text{max}}^{\text{Nujol}}$ 1714, 1730 (*infl.*) 3470 cm^{-1} , rotatory dispersion curve (MeOH) $[\Phi]_{350} -460^\circ$, $[\Phi]_{288} -1155^\circ$, $[\Phi]_{274} -1250^\circ$ (*infl.*), $[\Phi]_{267} -1310^\circ$, $[\Phi]_{241} -2710^\circ$, NMR: 333 (HC(7), b), 241 (HC(3), s), 222 ($\text{H}_3\text{COC}(15)$, s) cps.

Methyl 16-norisopimara-1,7-dien-2-ol-3-on-15-oate (9). Methyl 16-norisopimar-7-en-3 β -ol-2-on-15-oate (1.07 g) in acetic acid (10 ml) was treated with freshly prepared bismuth oxide (1.5 g) for 5 h at 100°. The reaction mixture was diluted with water (200 ml) and extracted with ether to give the diosphenol ester 9 (1.05 g), which on recrystallisation from aqueous methanol and hexane had m.p. 106–107°, $[\alpha]_D -59^\circ$ (CHCl_3 , c 1.1). (Found: C 72.1; H 8.7. $\text{C}_{20}\text{H}_{28}\text{O}_4$ requires: C 72.3; H 8.5). $\lambda_{\text{max}}^{\text{EtOH}}$ 267 $\text{m}\mu$ (ϵ 9400), $\lambda_{\text{max}}^{\text{EtOH/NaOH}}$ 214 $\text{m}\mu$ (ϵ 5600), 310 $\text{m}\mu$ (ϵ 6400), $\nu_{\text{max}}^{\text{Nujol}}$ 3415, 1723, 1675, 1664 cm^{-1} .

Methyl 16-norisopimar-7-en-3-on-15-oate (10). Araucarone (2 g), dissolved in methanol (100 ml) was treated with a solution of sodium periodate (2 g) in water (25 ml) for 2 h at room temperature. The reaction mixture was diluted with water (100 ml), acidified with sulphuric acid (10%, 100 ml) and extracted with chloroform. Removal of the solvent gave a crystalline residue (1.8 g, m.p. 168–175°) which was esterified with an ethereal solution of diazomethane. The product was chromatographed on silica gel (200 g) and

elution with isopropyl ether-hexane (3:2) gave the keto-ester (1.5 g), which on recrystallisation from aqueous methanol and hexane had m.p. 74–75°, $[\alpha]_D - 65^\circ$ (CHCl_3 , c 1.0). (Found: C 75.5; H 9.7. $\text{C}_{20}\text{H}_{30}\text{O}_3$ requires: C 75.4; H 9.5). $\lambda_{\text{max}}^{\text{EtOH}}$ 273 μm (ϵ 169), $\nu_{\text{max}}^{\text{Nujol}}$ 1712, 1732 cm^{-1} , NMR: 330 (HC(7), b), 223 ($\text{H}_3\text{COC}(15)$, s) cps, rotatory dispersion curve (MeOH) $[\Phi]_{314} - 2180^\circ$ (trough), $[\Phi]_{274} + 440^\circ$ (peak), $[\Phi]_{227} - 5320^\circ$.

Sodium borohydride reduction of methyl 16-norisopimar-7-en-3-on-15-oate (10). The keto-ester 10 (50 mg) in methanol (5 ml) was added to a solution of sodium borohydride (100 mg) in methanol (5 ml), which had been made slightly alkaline with a drop of aqueous sodium hydroxide (10 %). The reaction mixture was left overnight, diluted with water and extracted with ether. The solvent was removed to give the hydroxy-ester 11 (48 mg), which on recrystallisation from isopropyl ether had m.p. 103–105°, $[\alpha]_D - 23^\circ$ (CHCl_3 , c 0.8). $\nu_{\text{max}}^{\text{CS}_2}$ 817, 829, 860, 999, 1022, 1033, 1055, 1089, 1100, 1728, 3615 cm^{-1} . *p*-Nitrobenzoate m.p. 207–208°, $[\alpha]_D + 20^\circ$ (CHCl_3 , c 1.0). (Found: C 69.4; H 7.9. $\text{C}_{27}\text{H}_{36}\text{O}_6\text{N}$ requires: C 69.1; H 7.5).

Wolff-Kishner reduction of methyl 16-norisopimar-7-en-2-on-3 β -ol-15-oate (7). Methyl 16-norisopimar-7-en-2-on-3 β -ol-15-oate (600 mg) was added to a solution of potassium hydroxide (1.0 g) in diethylene glycol (10 ml, redistilled) and hydrazine hydrate (99–100 %, 0.8 ml). The reaction mixture was kept under nitrogen and the temperature gradually increased to 180° over 1 h. Water and excess hydrazine were removed by distillation at 195°. The reaction mixture was kept 4 h at 210–215° under nitrogen, cooled, diluted with water (200 ml), acidified with dilute sulphuric acid and extracted with ether. The product was esterified with an ethereal solution of diazomethane and the resulting ester mixture (480 mg) was chromatographed on silica gel (activity 1, 50 g). Hexane-isopropyl ether (10:1) eluted a mixture (337 mg) of methyl 16-norisopimar-7-en-15-oate (12) and methyl 16-norisopimar-2,7-dien-15-oate (13), which appeared homogeneous by thin layer chromatography. The mass spectrum of the mixture was nearly identical with that of 12, except for two minor peaks at m/e 302 (30 % of the intensity of m/e 304) and 287 and two prominent peaks at m/e 220 and 160. Similarly the NMR spectrum of the mixture was nearly identical with that of 12 differing mainly in the olefinic region (329 cps, s, 1.4 H), which showed a narrower peak superimposed on the C(7) proton band and indicating the presence of about 25 % of the diene. Elution with hexane-isopropyl ether (1:2) gave the hydroxy-ester 11 (142 mg), which on recrystallisation from hexane had m.p. 103–105°, undepressed on admixture with the hydroxy-ester obtained from araucarone. The infrared and NMR spectra of the two samples were identical.

Chromium trioxide oxidation of methyl 16-norisopimar-7-en-3 β -ol-15-oate (11). 16-Norisopimar-7-en-3-ol-15-oate (45 mg), dissolved in acetone (10 ml), was treated with a solution of chromium trioxide (25 mg) in aqueous sulphuric acid at room temperature for 30 min. Dilution with water followed by extraction with ether gave a product which was chromatographed on silica gel (15 g). Elution with hexane-isopropyl ether (3:2) gave the keto-ester 10 (35 mg), which on recrystallisation from aqueous methanol had m.p. 74–75°, undepressed on admixture with the keto-ester obtained from araucarone. The NMR spectra of the two samples were identical.

Methyl 16-norisopimar-7-en-15-oate (12). Methyl 16-norisopimar-7-en-3-on-15-oate (10) (500 mg) was added to a solution of potassium hydroxide (900 mg) in diethylene glycol (10 ml, redistilled) and hydrazine hydrate (99–100 %, 0.8 ml). The reaction mixture was kept under nitrogen and the temperature was gradually increased to 180° over 1 h. Water and excess hydrazine were removed by distillation at 200°. The reaction mixture was kept at 210–215° under nitrogen for 6 h, cooled to room temperature, diluted with water (200 ml), acidified with dilute sulphuric acid and extracted with ether. Removal of the ether gave the norketo acid (455 mg) which on recrystallisation from isopropyl ether had m.p. 193–195°. (Found: C 78.4; H 10.6. $\text{C}_{16}\text{H}_{22}\text{O}_2$ requires: C 78.6; H 10.4). Esterification with an ethereal solution of diazomethane and distillation at reduced pressure (0.1 mm) gave the ester 12, $[\alpha]_D + 13^\circ$ (CHCl_3 , c 1.9), n_D^{25} 1.515. (Found: C 78.6, H 10.7. $\text{C}_{20}\text{H}_{32}\text{O}_2$ requires: C 78.9; H 10.6). $\nu_{\text{max}}^{\text{film}}$ 820, 833, 857, 1670, 1732, NMR: 330 (HC(7), b), 223 ($\text{H}_3\text{COC}(15)$, s) cps.

Methyl 3 β -acetoxy-16-norisopimar-7-en-2-on-15-oate (30). The ketol ester 7 (2.1 g) dissolved in pyridine (10 ml) was treated with acetic anhydride (10 ml) at 40° for 20 h.

After addition of methanol (30 ml) the product (2.4 g) was taken to dryness, dissolved in isopropyl ether and filtered through alumina. Recrystallisation from aqueous methanol, hexane and isopropyl ether gave the ketol ester acetate, m.p. 120–122°, $[\alpha]_D + 32^\circ$ (CHCl_3 , c 1.0). (Found: C 70.4; H 8.6. $\text{C}_{22}\text{H}_{32}\text{O}_5$ requires: C 70.2; H 8.6). $\nu_{\text{max}}^{\text{Nujol}}$ 1245, 1723, 1751 cm^{-1} , rotatory dispersion curve (MeOH) $[\Phi]_{400} + 140^\circ$, $[\Phi]_{308} + 810^\circ$ (peak), $[\Phi]_{276} - 855^\circ$ (trough), $[\Phi]_{225} - 3755^\circ$.

Ethylene dithioketal of methyl 3 β -acetoxy-16-norisopimar-7-en-2-on-15-oate. To a solution of the ketol-ester acetate 30 (400 mg) in acetic acid (10 ml) and dithioglycol (2 ml) was added boron trifluoride etherate (2 ml). The reaction mixture was left for 4 h and poured into water (500 ml), neutralised with aqueous sodium hydroxide (10 %) and extracted with ether, to give the thioketal (540 mg), which on recrystallisation from hexane and isopropyl ether had m.p. 179–180°. (Found: C 63.6; H 8.2; S 14.5. $\text{C}_{24}\text{H}_{36}\text{O}_4\text{S}_2$ requires: C 63.7; H 8.0; S 14.2). $\nu_{\text{max}}^{\text{CCl}_4}$ 1165, 1195, 1650 (broad), 1732 (broad), 1650 (infl.) cm^{-1} . Saponification (10 % ethanolic KOH, 5 h reflux) followed by esterification (ethereal CH_3N_3) gave the corresponding thioketal hydroxy ester, m.p. 145–148°.

Reduction of ethylene dithioketal of methyl 16-norisopimar-7-en-2-on-3 β -ol-15-oate. The thioketal ester alcohol 14 (530 mg) was dissolved in acetone (20 ml) and treated with Raney nickel (2 g = 4 ml of an ethanolic suspension containing 50 % Raney nickel) for 45 min at reflux temperature. The reaction mixture was filtered, taken to dryness and chromatographed on silica gel (activity 1, 40 g) using hexane with an increasing amount of isopropyl ether for elution. Some of the fractions obtained were rechromatographed under the same conditions. The first fraction (45 mg) consisted of methyl 16-norisopimar-7-en-3-on-15-oate, m.p. and mixed m.p. 74–75°. The NMR spectrum was identical with that of the product obtained from araucarone on sodium periodate oxidation followed by esterification. The second fraction (10 mg) was starting material. The third fraction (35 mg) was an ester alcohol probably isomeric with 11. The fourth fraction (238 mg) was the expected product, methyl 16-norisopimar-7-en-3 β -ol-15-oate, m.p. and mixed m.p. 103–105°. The NMR spectrum was identical with that of authentic material.

Isopimar-7-ene-3 β ,15,16-triol (15). Araucarone (2.8 g), in ether (200 ml), was added to lithium hydrido-aluminate (3 g) in ether (300 ml) and boiled under reflux for 3 h. Excess lithium hydrido-aluminate was destroyed with ethyl acetate and the reaction product was diluted with water (300 ml) and acidified with dilute sulphuric acid. Removal of the ether from the combined ether extracts followed by recrystallisation from aqueous methanol and chloroform-methanol gave the triol 15 (2.5 g) m.p. 199–203°, $[\alpha]_D - 30^\circ$ (EtOH, c 1.0). $\nu_{\text{max}}^{\text{Nujol}}$ 917, 1025, 1044, 1057, 1086, 3330 cm^{-1} . Triacetate, m.p. 125–127°. (Found: C 69.6; H 9.3. $\text{C}_{26}\text{H}_{40}\text{O}_6$ requires: C 69.6; H 9.0).

16-Norisopimar-7-en-3 β -ol-15-al (16). The triol 15 (2.5 g), dissolved in methanol (100 ml), was treated with a solution of sodium periodate (3 g) in water (25 ml) for 1 h at room temperature. The reaction mixture was diluted with water (500 ml) and extracted with ether to give the hydroxy aldehyde (2.2 g), which on recrystallisation from aqueous methanol and isopropyl ether had m.p. 145–146°, $[\alpha]_D - 38^\circ$ (CHCl_3 , c 2.0). (Found: C 78.3; H 10.5. $\text{C}_{19}\text{H}_{32}\text{O}_2$ requires: C 78.6; H 10.4). $\nu_{\text{max}}^{\text{CS}_2}$ 910, 998, 1040, 1090, 1726, 2695, 3615 cm^{-1} , NMR: 569 (HC(15), s), 329 (HC(7), b) cps.

16-Norpimar-7-en-3 α -ol and 16-norpimar-7-en-3 β -ol (17). Crude 16-norisopimar-7-en-3-ol-15-al (800 mg), obtained from araucarone on reduction with lithium hydrido-aluminate followed by oxidation with sodium periodate without purification, was added to a solution of potassium hydroxide (1.5 g) in diethylene glycol (15 ml, redistilled) and hydrazine hydrate (99–100 %, 1.5 ml). The reaction mixture was kept under nitrogen and the temperature was gradually increased to 180° over 1 h. Water and excess hydrazine were removed by distillation at 190°. The reaction mixture was kept at 210–215° under nitrogen for 4 h, cooled to room temperature, diluted with water (200 ml), acidified with dilute sulphuric acid and extracted with ether. The product was chromatographed on alumina (40 g). Elution with hexane-isopropyl ether (1:2) gave 16-norpimar-7-en-3 α -ol, (65 mg) which on recrystallisation from isopropyl ether had m.p. 110–111°, $[\alpha]_D - 51^\circ$ (CHCl_3 , c 2.2). (Found: C 82.6; H 11.8. $\text{C}_{19}\text{H}_{32}\text{O}$ requires: C 82.5; H 11.7). $\nu_{\text{max}}^{\text{CS}_2}$ 919, 981, 1002, 1021, 1047, 1091, 3630 cm^{-1} , NMR: 325 (HC(7), b), 210 (HC(3), b) cps.

Elution with isopropyl ether gave 16-norpimar-7-en-3 β -ol, (520 mg), which on recrystallisation from isopropyl ether had m.p. 157–158°, $[\alpha]_D -56^\circ$ (CHCl₃, *c* 2.1). (Found: C 82.8; H 12.1. C₁₉H₃₂O requires: C 82.5; H 11.7). $\nu_{\max}^{\text{CS}_2}$ 916, 939, 972, 984, 1059, 3640 cm⁻¹, NMR: 324 (HC(7), b), 196 (HC(3), q, *J* 5, 9) cps. The *p*-nitrobenzoate, prepared by treatment of the equatorial alcohol with excess *p*-nitrobenzoyl chloride in pyridine at 40° for 15 h, on recrystallisation from ethanol had m.p. 193–194°, $[\alpha]_D + 23^\circ$ (CHCl₃, *c* 2.3). (Found: C 73.3; H 8.3; N 3.3. C₂₆H₃₅O₄N requires: C 73.4; H 8.3; N 3.3).

16-Norpimar-7-en-3-one (18). 16-Norpimar-7-en-3 β -ol (495 mg), dissolved in acetone (20 ml), was treated with a solution of chromium trioxide (160 mg) in aqueous sulphuric acid (10%, 2 ml) at room temperature for 30 min. Dilution with water followed by extraction with ether gave the ketone 18 (480 mg), which on recrystallisation from methanol had m.p. 117–118°. (Found: C 82.9; H 11.1. C₁₉H₃₀O requires: C 83.2; H 11.0). Mol.wt. 274 (mass spectrum). ν_{\max}^{EtOH} 273 μ (ϵ 169), $\nu_{\max}^{\text{Nujol}}$ 838, 1711 cm⁻¹, NMR: 325 (HC(7), b), cps. Rotatory dispersion curve (MeOH) $[\Phi]_{500} -330^\circ$, $[\Phi]_{314} -2310^\circ$ (trough), $[\Phi]_{274} 0^\circ$ (peak), $[\Phi]_{231} -5440^\circ$.

Oxidation of 16-norpimar-7-en-3 α -ol (12 mg) in the above manner also furnished the ketone 18 (10 mg), m.p. and mixed m.p. 117–118°. The infrared spectra were identical.

16-Norpimar-7-ene (19). 16-Norpimar-7-en-3-one (200 mg) was added to a solution of potassium hydroxide (400 mg) in diethylene glycol (10 ml, redistilled) and hydrazine hydrate (99–100%, 0.5 ml). The reaction mixture was kept under nitrogen and the temperature was gradually increased to 180° over 1 h. Water and excess hydrazine was removed by distillation at 190°. The reaction mixture was kept at 205–210° for 11 h under nitrogen, cooled to room temperature, diluted with water (200 ml), acidified with dilute sulphuric acid and extracted with hexane. The hydrocarbon (172 mg), on recrystallisation from acetone, had m.p. 43–44°, $[\alpha]_D -27^\circ$ (CHCl₃, *c* 1.4), NMR: 322 (HC(7), b) cps. A comparison of this hydrocarbon, kindly made by Dr. Ireland, with 16-norpimar-7-ene (13,13-dimethylpodocarp-7-ene) previously obtained by him from isopimaric acid showed the two compounds to be identical by mixed m.p. 43–44°. (Dr. Ireland has informed us that the earlier reported m.p. 29–31° of this compound has been raised to 44–44.5° by recrystallisation). The infrared spectra were also identical.

Isopimara-7,15-dien-3 β -ol (20). To triphenylmethylphosphonium bromide (5.3 g) in anhydrous ether (75 ml) was added a solution of potassium *t*-butoxide in *t*-butyl alcohol (0.95–1.0 M, 14 ml) and the mixture was stirred for 1 h under nitrogen. The hydroxy-aldehyde 16 (980 mg), dissolved in ether (25 ml), was added and the reaction mixture was stirred for 5 h at 20° under nitrogen. Dilution with water and extraction with ether gave a product (2.1 g, triphenylphosphonium oxide and alcohol), which was chromatographed on alumina (activity 1, 60 g). Elution with ether-isopropyl ether (1:1) gave the diene alcohol 20 (870 mg), which on recrystallisation from isopropyl ether had m.p. 146–147°, $[\alpha]_D -36^\circ$ (CHCl₃, *c* 1.8). $\nu_{\max}^{\text{CS}_2}$ 817, 831, 910, 997, 1027, 1052, 1090, 1638, 3615 cm⁻¹, NMR: 326 (HC(7), b), 347 (HC(15), q, *J* 10, 18), 290 (H_{cis}C(16), q, *J* 10, 2), 293 (H_{trans}C(16), q, *J* 18, 2), 197 (HC(3), q, *J* 9, 5) cps. *p*-Nitrobenzoate, m.p. 178–179°, $[\alpha]_D + 32^\circ$ (CHCl₃, *c* 0.9). (Found: N 3.2. C₂₇H₃₅O₄N requires: N 3.2).

Isopimara-7,15-dien-3-one (21). Isopimara-7,15-dien-3 β -ol (650 mg) in acetone (18 ml) was treated with a solution of chromium trioxide (200 mg) in aqueous sulphuric acid (10%, 2.5 ml) for 30 min at 20°. The reaction mixture was diluted with water (200 ml) and extracted with ether to give the diene ketone (640 mg), which on recrystallisation from methanol had m.p. 91–92°, $[\alpha]_D -82^\circ$ (CHCl₃, *c* 2.0). (Found: C 83.6; H 10.6. C₂₀H₃₀O requires: C 83.9; H 10.6). $\nu_{\max}^{\text{Nujol}}$ 841, 907, 1637, 1714 cm⁻¹.

Isopimara-7,15-diene (22). Isopimara-7,15-dien-3-one (300 mg) was added to a solution of potassium hydroxide (600 mg) in diethylene glycol (10 ml, redistilled) and hydrazine hydrate (99–100%, 0.8 ml). The reaction mixture was kept under nitrogen and the temperature was gradually increased to 180° over 1 h. Water and excess hydrazine was removed by distillation at 190°. The reaction mixture was kept at 205–210° for 6 h under nitrogen, cooled to 20°, diluted with water (200 ml), acidified with dilute sulphuric acid and extracted with hexane. Removal of the solvent followed by distillation of the product (280 mg) at reduced pressure (0.2 mm) gave the diene 22, $[\alpha]_D -33^\circ$ (CHCl₃, *c* 4.4). The identity of this diene with that previously obtained from isopimaric acid was

established by comparison, kindly made by Dr. Ireland, of the infrared and NMR spectra, which were identical.

16-Norpimar-3 β -ol and 8 β -16-norpimar-3 β -ol (23). 16-Norpimar-7-en-3 β -ol (500 mg) was hydrogenated over a platinum oxide catalyst (25 mg) in acetic acid (10 ml) at room temperature until uptake ceased after 4 h. The product on repeated recrystallisation from methanol gave 8 β -16-norpimar-3 β -ol (160 mg), m.p. 132–133°, $[\alpha]_D + 18^\circ$ (CHCl₃, *c* 2.1). (Found: C 82.2; H 12.5. C₁₉H₃₄O requires: C 82.0; H 12.3). Mol. wt. 278 (mass spectrometry). Repeated crystallisation of the first mother liquor from aqueous ethanol gave 16-norpimar-3 β -ol (15 mg), m.p. 153–154°. (Found: C 82.1; H 12.6. C₁₉H₃₄O requires: C 82.0; H 12.3). Mol. wt. 278 (mass spectrometry).

8 β -16-norpimar-3-one (24) and 16-norpimar-3-one. 8 β -16-norpimar-3 β -ol (30 mg) in acetone was treated with a solution of chromium trioxide (15 mg) in aqueous sulphuric acid (10 %, 0.5 ml) at room temperature for 30 min. Dilution with water followed by extraction with ether gave 8 β -16-norpimar-3-one 24 (25 mg), which on recrystallisation from methanol had m.p. 105–106°. (Found: C 82.9; H 12.1. C₁₉H₃₂O requires: C 82.5; H 11.7). Mol. wt. 276 (mass spectrometry). ν_{\max}^{KBr} 1689 cm⁻¹, rotatory dispersion curve: $[\Phi]_{400} + 205^\circ$, $[\alpha]_{303} + 1565^\circ$ (peak), $[\Phi]_{265} - 485^\circ$ (trough), $[\Phi]_{224} + 225^\circ$.

Oxidation of 16-norpimar-3 β -ol (8 mg) under the same conditions gave the liquid 16-norpimar-3-one (7 mg), which after filtration through silica gel in hexane followed by distillation had mol. wt. 276 (mass spectrometry), ν_{\max}^{Film} 1704 cm⁻¹. It gave a mass spectrum practically identical with that of the 8-epimer 24.

Phosphorus pentachloride rearrangement of 8 β -16-norpimar-3 β -ol (23). 8 β -16-norpimar-3 β -ol (230 mg) in hexane (10 ml) was concentrated to half volume, cooled in an icebath and treated with excess PCl₅ for 1 h. The reaction mixture was then concentrated to a small volume under reduced pressure, filtered through alumina and evaporated giving an oil (173 mg) which could not be crystallised. The oil was ozonised in methylene chloride (10 ml) at -70° until the solution remained blue. The reaction mixture was warmed to slightly above room temperature and a stream of nitrogen was passed through the solution and then through a dinitrophenylhydrazine trap. The product from the trap was filtered through alumina and the crude dinitrophenylhydrazone (45 mg) was chromatographed on silica gel and recrystallised three times from ethanol giving acetone dinitrophenylhydrazone, m.p. and mixed m.p. 125–126°. A blank ozonolysis gave 13 mg of crude dinitrophenylhydrazone product that was shown by thin layer chromatography to contain no acetone dinitrophenylhydrazone.

The main ozonolysis product remaining after blowing off the solvent and other volatile material was heated on the water bath with zinc and acetic acid for 20 min. It was then taken up in ether, and the ethereal solution was washed with alkali and evaporated and the product was chromatographed on silica gel with hexane-ether mixtures. This gave 65 mg of non-crystalline fractions with strong infrared absorption at 1742 cm⁻¹.

3,16-Bisnorisopimar-7-en-2 α -carboxy-2 β -ol-15-oic acid (27). The diosphenol ester 9 (405 mg) was added to a mixture of ethanol (15 ml) and aqueous sodium hydroxide (10 %, 12 ml) and boiled under reflux for 6 h. The reaction mixture was cooled, diluted with hydrochloric acid (10 %, 150 ml) and extracted with ether to give the di-acid alcohol 27 (410 mg), which on recrystallisation from acetone had m.p. 279–280°. (Found: C 67.9; H 8.8. C₁₉H₂₈O₅ requires: C 67.8; H 8.4). $\nu_{\max}^{\text{Nujol}}$ 1698, 1716, 2500–2800, 3485 cm⁻¹.

3,16-Bisnorisopimar-7-en-2 α -carbinol-2 β ,15-diol (28). The hydroxy-diacid 27 (230 mg) in dioxan (10 ml) was added to lithium hydrido-aluminate (300 mg) in dioxan-ether (1:1, 30 ml) and the resulting mixture boiled under reflux for 5 h. Excess lithium hydrido-aluminate was destroyed with ethyl acetate and after addition of water and dilute hydrochloric acid the reaction mixture was extracted with ether. Removal of the solvent gave the triol 28 (211 mg) which on recrystallisation from acetone had m.p. 198–199° (decomp.). (Found: C 74.0; H 10.8. C₁₉H₃₂O₃ requires: C 74.0; H 10.5).

3,16-Bisnorisopimar-7-en-15-ol-2-one (29). The triol 28 (100 mg) in ethanol (20 ml) was treated with a solution of sodium periodate (200 mg) in water (3 ml) for 1.5 h at 20°. The reaction mixture was diluted with water and extracted with ether and the crude product (90 mg) was chromatographed on silica gel (10 g). Elution with isopropyl ether gave the A-norketo-alcohol 29 (51 mg), which on recrystallisation from aqueous methanol and hexane/isopropyl ether had m.p. 140–141°. (Found: C 78.4; H 10.5. C₁₈H₂₈O₂ requires:

C 78.2; H 10.2). ν_{\max}^{CCl} 1416, 1649, 1741, 3450, 3655 cm^{-1} , NMR: 333 (HC(7), b), 201 (HC(15), s) cps.

Rotatory dispersion curve (MeOH): $[\Phi]_{400} + 765^\circ$, $[\Phi]_{314} + 7500^\circ$ (peak), $[\Phi]_{263} - 7480^\circ$ (trough), $[\Phi]_{258} - 7300^\circ$, $[\Phi]_{234} - 6010^\circ$, $[\Phi]_{228} - 7350^\circ$, $[\Phi]_{214} - 15\ 200^\circ$ (trough), $[\Phi]_{209} - 9300^\circ$.

Methyl 16-norisopimar-7-en-2-on-15-oate (31). Methyl 3 β -acetoxy-16-norisopimar-7-en-2-on-15-oate (500 mg) in toluene (5 ml, concentrated from 10 ml to remove water) was added to a solution of calcium (300 mg) in liquid ammonia (30 ml, distilled over sodium) over 5 min with stirring. The reaction mixture was stirred for 10 min and bromobenzene was added followed by water. The ammonia was distilled off and the non-volatile material was diluted with water, extracted with ether and chromatographed on silica gel (60 g). Elution with isopropyl ether gave the keto ester 31 (183 mg), which on recrystallisation from aqueous methanol had m.p. 89–90°. (Found: C 75.3; H 9.8. $\text{C}_{20}\text{H}_{30}\text{O}_5$ requires: C 75.4; H 9.6). $\lambda_{\max}^{\text{EtOH}}$ 285 μ (ϵ 38), $\nu_{\max}^{\text{Nujol}}$ 1721, 1737 cm^{-1} , rotatory dispersion curve (MeOH): $[\Phi]_{392} - 12^\circ$, $[\Phi]_{309} + 860^\circ$ (peak), $[\Phi]_{265} - 2900^\circ$, $[\Phi]_{260} - 3030^\circ$ (trough), $[\Phi]_{255} - 3100^\circ$, $[\Phi]_{238} - 3610^\circ$, $[\Phi]_{224} - 6100^\circ$, $[\Phi]_{207} - 23\ 800^\circ$; NMR: 333 (HC(7), b), 209 (H₂C(15), s), 140 (H₂C(1), s) cps.

Lithium hydrido-aluminate reduction of araucarol (32). Araucarol (50 mg) in ether (10 ml) was added to lithium hydrido-aluminate (200 mg) in ether (30 ml) and boiled under reflux for 3 h. The product was worked up as usual to give isopimar-7-ene-3 β ,15,16-triol (50 mg), m.p. and mixed m.p. 199–203°, infrared spectrum superimposable on that of authentic material.

Sodium periodate oxidation of araucarol (32). Araucarol (150 mg) in methanol (15 ml) was treated with a solution of sodium periodate (200 mg) in water (3 ml) for 3 h at 20°. The reaction mixture was diluted with water (100 ml), acidified with dilute sulphuric acid and extracted with ether to give crude hydroxy-acid (134 mg), which was esterified with an ethereal solution of diazomethane, and chromatographed on alumina (20 g). Ether eluted methyl 16-norisopimar-7-en-3 β -ol-15-oate (93 mg), m.p. and mixed m.p. 103–105°, infrared spectrum superimposable on that of authentic material.

16-Acetoxy-isopimar-7-ene-2,15-dione-3 β -ol (33). Araucarolone (500 mg) was added to a solution of acetic anhydride (2.5 ml) and pyridine (2.5 ml) and left for 15 min at room temperature. Dilution with water (100 ml) followed by extraction with ether gave the monoacetate, which on recrystallisation from isopropyl ether had m.p. 140–141°, $[\alpha]_{\text{D}} - 33^\circ$ (CHCl_3 , c 23). (Found: C 70.3; H 8.9. $\text{C}_{22}\text{H}_{32}\text{O}_5$ requires: C 70.2; H 8.6). Mol. wt. 376 (mass spectrometry), $\nu_{\max}^{\text{Nujol}}$ 1238, 1714, 1749, 3475 cm^{-1} , NMR: 338 (HC(7), b) 298 (H₂C(16), s) 242 (HC(3), d, J 5), 136 (H₃CCOO, s) cps.

Preparation of araucarenolone (34). 16-Acetoxy-isopimar-2,15-dione-3 β -ol (50 mg) was added to a solution of bismuth oxide (50 mg) in acetic acid (3 ml) and kept at 100° for 1 h. Dilution with water and extraction with ether gave a gum, which was treated with a mixture of ethanol (4 ml) and aqueous sodium hydroxide (0.6 ml 0.1 M), under nitrogen at room temperature for 1 h. The reaction mixture was acidified with acetic acid and extracted with ether. The ether extract after washing with saturated aqueous sodium hydrogen carbonate and water gave araucarenolone (32 mg), which on repeated recrystallisation from ethanol had m.p. and mixed m.p. 143–144°. The NMR spectrum was identical with that of the naturally occurring compound.

Perphthalic acid oxidation of araucarolone diacetate (4). Araucarolone diacetate (1.20 g) in dry ether (100 ml) was added to an ethereal solution of monophrthalic acid (0.27 M, 400 ml) and left in a dark place at room temperature for a week. The solution was washed with a saturated aqueous solution of sodium hydrogen carbonate and with water. The product was chromatographed on silica gel (150 g) using an isopropyl ether-ether gradient. Some of the intermediate fractions, which according to thin layer chromatograms contained two components, were rechromatographed under identical conditions.

The first fraction was 3 β -acetoxy-15,16-bisnorisopimaran-2-on-7 β ,8 β -oxido-13 α -ol acetoxyacetate 37 (349 mg), which on recrystallisation from aqueous methanol had m.p. 140–141°, $[\alpha]_{\text{D}} + 12^\circ$ (CHCl_3 , c 1.2). (Found: C 64.1; H 7.9. $\text{C}_{24}\text{H}_{34}\text{O}_8$ requires: C 64.0; H 7.6). $\nu_{\max}^{\text{Nujol}}$ 1075, 1197, 1216, 1245, 1720, 1747, 1756 (infl.) cm^{-1} . This compound was also formed on treatment of 7 β ,8 β -oxido-araucarolone diacetate with monophrthalic acid in ether, as demonstrated by thin layer chromatography.

The second fraction was β ,8-acetoxy-15,16-bisnorisopimarane-2-on-7 α ,8 α -oxido-13 α -ol acetoxyacetate 36 (235 mg), which on recrystallisation from methanol had m.p. 195–196°, $[\alpha]_D + 5^\circ$ (CHCl₃, *c* 1.2). (Found: C 64.0; H 7.8. C₂₄H₃₄O₈ requires: C 64.0; H 7.6). $\nu_{\max}^{\text{Nujol}}$ 1071, 1190, 1230, 1730, 1745, 1757 cm⁻¹. This compound was also formed on treatment of 7 α ,8 α -oxido-araucarolone diacetate with monopero-phthalic acid in ether, as demonstrated by thin layer chromatography.

The third fraction was a mixture of 7 β ,8 β -oxido-araucarolone diacetate 35 (102 mg) and 7 α ,8 α -oxido-araucarolone diacetate 5 (503 mg), which was readily separated by crystallisation from methanol. The β -epoxide 35 had m.p. 168–170°, $[\alpha]_D + 16^\circ$ (CHCl₃, *c* 1.0). (Found: C 66.3; H 7.9. C₂₄H₃₄O₇ requires: C 66.3; H 7.9). $\nu_{\max}^{\text{Nujol}}$ 1039, 1080, 1235, 1723, 1744 cm⁻¹. The liquid α -epoxide 5 had $[\alpha]_D + 50^\circ$ (CHCl₃, *c* 1.1). (Found: C 66.5; H 8.3. C₂₄H₃₄O₇ requires: C 66.3; H 7.9). ν_{\max}^{Film} 1042, 1092, 1717, 1739 cm⁻¹.

Perphthalic acid oxidation of 16-norpimar-7-ene (19). 16-Norpimar-7-ene (2.1 g) in dry ether (100 ml) was treated with an ethereal solution of monopero-phthalic acid (0.27 M, 200 ml) at room temperature in the dark for 48 h. The ether solution was washed with a saturated aqueous solution of sodium hydrogen carbonate and with water. The product (2.25 g), according to thin layer chromatography on silica gel, was a 1:3 mixture of two epoxides of similar *R_F*. These were separated on a preparative scale by chromatography on alumina (activity 2, 80 g) using a hexane-isopropyl ether gradient. The faster moving minor component was 16-norpimarane-7 β ,8 β -oxide (40), which on recrystallisation from methanol had m.p. 98–99°, mol. wt. 276 (mass spectrometry). (Found: C 82.8; H 12.0. C₁₉H₃₂O requires: C 82.5; H 11.7). NMR: 175 (HC(7), d, *J* 6) cps. The slower moving major component was 16-norpimarane-7 α ,8 α -oxide (39), which on recrystallisation from methanol had m.p. 61–62° changing on standing to 83–84°, mol. wt. 276 (mass spectrometry). (Found: C 82.5; H 11.7. C₁₉H₃₂O requires: C 82.5; H 11.7). NMR: 175 (HC(7), d, *J* 1.4) cps.

These epoxides were very sensitive to acid, the β -epoxide converting to hydrocarbon and the α -epoxide to a mixture of allyl alcohols. Preparative chromatography always gave some conversion to the allyl alcohols depending on the conditions and the time taken for separation. When spotted on silica gel thin layer plates in the presence of perphthalic acid the epoxides were immediately converted to other products. The perphthalic acid oxidation mixture could, however, be chromatographed satisfactorily by spotting on top of spots of saturated sodium hydrogencarbonate solution.

The faster moving of the allyl alcohols was 16-norpimar-8(9)-en-7 α -ol (45), which on recrystallisation from isopropyl ether and sublimation (110°, 0.1 mm) had m.p. 123–124°. (Found: C 82.3; H 11.7. C₁₉H₃₂O requires: C 82.5; H 11.7). NMR: 232 (HC(7), b) cps. The slower moving of the allyl alcohols was 16-norpimar-8(14)-en-7 α -ol (46), which on recrystallisation from methanol had m.p. 105–108°. (Found: C 82.4; H 11.9. C₁₉H₃₂O requires: C 82.5; H 11.7). NMR: 329 (HC(14), s), 251 (HC(7), b) cps.

Ozonolysis of 16-norpimar-7-ene (19). 16-Norpimar-7-ene (500 mg) in ethyl acetate (40 ml) was treated with ozone at –70° until excess ozone was present as indicated by a permanent blue colour. The solution was poured onto a mixture of zinc (4 g) and acetic acid (4 ml) and left over night. The product was taken up in ether and washed with saturated aqueous sodium hydrogen carbonate and water and chromatographed on silica gel (80 g) using a hexane-isopropyl ether gradient. Some fractions were rechromatographed under identical conditions.

The first fraction (16 mg), according to its NMR spectrum, was largely 16-norpimarane-7,9(11)-diene and was not further investigated. The second fraction (79 mg) was 16-norpimarane-7 α ,8 α -oxide (39), which on recrystallisation from methanol had m.p. and mixed m.p. 61–62° and gave an NMR spectrum identical with that of authentic material. The third fraction (214 mg) was 16-norpimar-8(9)-en-7 α -ol (45), which on sublimation had m.p. and mixed m.p. 123–124°, NMR spectrum identical with that of authentic material. Attempts to recrystallise part of this fraction from methanol prior to sublimation gave 7-methoxy-16-norpimar-8(9)-ene, identified by NMR. The fourth fraction (69 mg) was 16-norpimar-8(14)-en-7 α -ol (46), which on recrystallisation from methanol had m.p. and mixed m.p. 98–99°, NMR spectrum identical with that of authentic material. The fifth fraction (23 mg) was the seco-keto aldehyde 38, which was not obtained completely pure and was characterised by its NMR spectrum only.

A small portion of the crude ozonolysis product, allowed to warm to room temperature and then evaporated to dryness, gave an NMR spectrum almost indistinguishable from that of 16-norpimarane-7 α ,8 α -oxide.

Lithium/ethylamine reduction of 16-norpimarane-7 α ,8 α -oxide (39). 16-Norpimarane-7 α ,8 α -oxide (260 mg) was added to lithium (200 mg) in ethylamine (30 ml), which had been stirred for 15 min. The reaction mixture was stirred for 15 min, ethanol (0.2 ml) was added and the stirring was continued for 1 h. After addition of ammonium chloride, evaporation of the ethylamine and dilution with water the product was extracted with ether and chromatographed on silica gel (30 g). Elution with hexane-isopropyl ether (7:1) gave 16-norpimarane-7 α -ol, 41, (250 mg), which on recrystallisation from aqueous methanol followed by sublimation (100°, 0.1 mm) had m.p. 106–107°. (Found: C 81.9; H 12.7. C₁₉H₃₄O requires: C 82.0; H 12.3). [α]_D –24°(CHCl₃, c 2.4), NMR: 228 (HC(7), b) cps. Mol. wt. 278 (mass spectrometry).

16-Norpimarane-7-one(44) and 6,6,8-d₃-16-norpimarane-7-one. 16-Norpimarane-7 α -ol (100 mg) in acetone (10 ml) was treated with a solution of chromium trioxide (40 mg) in aqueous sulphuric acid (10 %, 1 ml) at room temperature for 15 min. The reaction mixture was diluted with water and extracted with ether to give 16-norpimarane-7-one, 44, (96 mg), which on recrystallisation from methanol followed by sublimation (130°, 0.1 mm) had m.p. 147–148°. (Found: C 82.4; H 11.7. C₁₉H₃₂O requires: C 82.5; H 11.7), mol. wt. 276 (mass spectrometry). This ketone was recovered unchanged, after treatment with ethanolic potassium hydroxide (10 %) at reflux temperature for 30 min under nitrogen.

16-Norpimarane-7-one (10 mg) was added to a solution prepared from sodium (10 mg) and 0-deutero-ethanol (2 ml, 95 %) and kept under nitrogen at reflux temperature for 60 min. After removal of the solvent the procedure was repeated twice with fresh solvent. Dilution with deuterium oxide (2 ml), extraction with dry ether and sublimation of the product gave 6,6,8-d₃-16-norpimarane-7-one (ca. 2/3 trideuterated and 1/3 dideuterated material), m.p. 146–147°, undepressed on admixture with starting material. Mol. wt. 279 (mass spectrometry).

Lithium hydrido-aluminate reduction of 16-norpimarane-7-one (44). 16-Norpimarane-7-one (10 mg) in dry ether (3 ml) was added to lithium hydrido-aluminate (50 mg) in ether (3 ml) and kept at reflux temperature for 30 min. Work up in the usual way gave crude 16-norpimarane-7 β -ol, 43 (10 mg) which was purified by chromatography on silica gel, recrystallisation from aqueous methanol and distillation, m.p. 80–81°. (Found: C 82.2; H 12.5. C₁₉H₃₄O requires: C 82.0; H 12.3). [α]_D +31°(CHCl₃, c 2.5), mol. wt. 278 (mass spectrometry), NMR: 193 (HC(7), sextet, J 11, 5, 11) cps.

Lithium/ethylamine reduction of 16-norpimarane-7 β ,8 β -oxide (40). 16-Norpimarane-7 β ,8 β -oxide (90 mg) was reduced under the same conditions as those used for the α -epoxide. The product was chromatographed on silica gel (15 g) using a hexane-ether gradient. The first fraction was 16-norpimarane-8 β -ol, 42 (76 mg), which on recrystallisation from aqueous methanol had m.p. 56–57°, mol. wt. 278 (mass spectrometry), NMR: 68 and 61 (H₃C(17), s, and H₃C(18), s), 53 (H₃C(15), H₃C(19) and H₃C(20), s) cps. The second fraction was 16-norpimarane-7 β -ol (43), m.p. and mixed m.p. 80–81°, NMR spectrum identical with that of authentic material.

16-Norpimar-8(9)-en-7-one (47). 16-Norpimar-8(9)-en-7 α -ol (20 mg) in acetone (5 ml) was treated with chromium trioxide (20 mg) in water (1 ml) for 15 min at room temperature. Aqueous sulphuric acid (3 %, 1 ml) was added and the mixture was stirred for 15 min. After dilution with water the mixture was extracted with ether and the product obtained was chromatographed on silica gel (5 g). Elution with isopropyl ether-hexane (1:10) gave 16-norpimar-8(9)-en-7-one (12 mg), which on recrystallisation from methanol had m.p. 102–103°. (Found: C 82.7; H 11.1. C₁₉H₃₀O requires: C 83.2; H 11.0). $\lambda_{\max}^{\text{EtOH}}$ 247 μ (ϵ 10 000), mol. wt. 274 (mass spectrometry).

16-Norpimar-8(9)-en-7 β -ol (48). 16-Norpimar-8(9)-en-7-one (55 mg) in ether (5 ml) was added to lithium hydrido-aluminate (90 mg) in ether (5 ml) and kept at reflux temperature for 30 min. Work up in the usual way gave crude 16-norpimar-8(9)-en-7 β -ol (50 mg), which was purified by chromatography on silica gel and sublimation, m.p. 107–110°. (Found: C 82.8; H 12.1. C₁₉H₃₂O requires: C 82.5; H 11.7). Mol. wt. 276 (mass spectrometry), NMR: 237 (HC(7), b) cps.

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