310. *Triterpenoids. Part VI.* Some Observations on the Constitution of Zeorin.*

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The saturated triterpenoid diol, zeorin, $C_{30}H_{52}O_2$, isolated from *Nephroma arcticum* L., has been fully characterised. Dehydration of the acetate afforded zeorinin acetate or *iso*zeorinin acetate according to the reagent used. The last ester contains an exocyclic methylene group or its equivalent. Hydrogenation of *iso*zeorin acetate, or hydrogenolysis of zeorin acetate, gave deoxyzeorin acetate. The carbonyl group of deoxyzeorinone and of zeorininone is very hindered; on the basis of infra-red evidence it is contained in a six-membered ring.

Dehydration of deoxyzeorin by toluene-*p*-sulphonyl chloride in pyridine, or pyrolysis of deoxyzeorin benzoate, afforded mixtures of hydrocarbons, converted by hydrogenation and further treatment into the saturated zeorinane. The latter is not identical with any known triterpenoid hydrocarbon.

The classical work of Zopf (*Annalen*, 1909, **364**, 273, and earlier papers) and of Hesse (*J. pr. Chem.*, 1906, **73**, 113) on the constituents of lichens led to the recognition of zeorin as a frequent component of these primitive organisms. For many years the chemistry of zeorin received little attention, until Asahina and Akagi (*Ber.*, 1938, **71**, 980) and Asahina and Yosioka (*ibid.*, 1940, **73**, 742) demonstrated that it was a pentacyclic secondary-tertiary diol, $C_{30}H_{52}O_2$, of the triterpenoid series. Through the kindness of Professor and Mrs. N. A. Sörensen (Trondheim, Norway) in collecting and making available to us a quantity of the lichen *Nephroma arcticum* L., it became possible for us to undertake a further study of zeorin.

Zeorin and a number of its simple derivatives do not exhibit sharp melting points. Our attention was first directed to a verification of the homogeneity of these compounds. This was established by thorough chromatographic fractionation of the acetate and of the benzoate. Oxidation of zeorin by chromic acid afforded zeorinone. This ketone showed infra-red carbonyl maxima at 5·86 μ (in carbon disulphide) and at 5·87 μ (in chloroform), values which are indicative (cf. R. Norman Jones *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 2024) of a keto-group in a six-membered ring. Zeorinone was resistant to the ordinary carbonyl characterising reagents.

Treatment of zeorin acetate with ethanolic hydrochloric acid (Zopf, *Annalen*, 1895, **288**, 50; Asahina and Yosioka, *loc. cit.*) led to dehydration, with formation of the long known zeorinin acetate. The far ultra-violet absorption spectrum of this compound (see Experimental section) indicated that the double bond was of either a tri- or a tetra-substituted type for which reference data are not yet available. Zeorinin acetate was further characterised by hydrolysis to zeorinin and by conversion of the latter into its benzoate. Treatment of zeorinin acetate with perhydrol in acetic acid gave the saturated zeorinin acetate oxide. The benzoate was prepared likewise and, on treatment with hydrochloric–acetic acids, furnished, with loss of water, dehydrozeorinin benzoate. The latter was identified as a conjugated diene by its absorption spectrum ($\lambda_{max.}$ 252 mμ; $\varepsilon_{max.} = 18{,}000$).

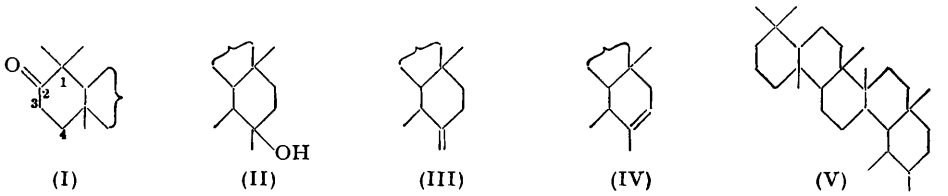
Zeorin acetate was dehydrated by phosphorus oxychloride in pyridine to a strongly dextrorotatory isomer of zeorinin acetate, which we designate *iso*zeorinin acetate. This was further characterised by hydrolysis to *iso*zeorinin and by benzoylation of the latter. Similar dehydration of zeorinone gave *iso*zeorininone. On digestion with ethanolic hydrochloric acid *iso*zeorininone was isomerised to zeorininone, also prepared, although in poor yield, by chromic acid oxidation of zeorinin; *iso*zeorinin benzoate was likewise isomerised to zeorinin benzoate. The infra-red spectrum of *iso*zeorinin acetate showed a strong band at 11·28 μ (in carbon disulphide), indicative of an exocyclic (or other) methylene

* Part V, *J.*, 1952, 78.

grouping ($>C{=}CH_2$), which band is not present in the infra-red spectrum of zeorinin acetate or of zeorinone. We conclude that zeorin contains the grouping $>CMe{\cdot}OH$. The " anhydrozeorin acetate," prepared by Asahina and Yosioka (*loc. cit.*) by refluxing zeorin with acetic acid, was probably somewhat impure *iso*zeorinin acetate.

Although Asahina and Yosioka (*loc. cit.*) claimed that zeorinin acetate could be hydrogenated to a " deoxyzeorin acetate " with a palladium catalyst, we have been unable to effect this reduction using a platinum catalyst even under vigorous conditions. *iso*-Zeorinin acetate, on the other hand, was smoothly hydrogenated, to deoxyzeorin acetate, also obtained by hydrogenolysis of zeorin acetate itself. Deoxyzeorin acetate was further characterised by hydrolysis to the alcohol and by conversion into the benzoate. Our series of deoxyzeorin compounds is not identical with the compounds prepared by Asahina and Yosioka (*loc. cit.*). Chromic acid oxidation of deoxyzeorin afforded deoxyzeorininone.

The carbonyl group in zeorinone, zeorininone, and in deoxyzeorinone cannot be situated at the usual $C_{(2)}$ position (as I) in the customary pentacyclic triterpenoid nucleus, because it is resistant to carbonyl reagents and to reduction. Thus Wolff–Kishner and Clemmensen reduction, even under such vigorous conditions as in the preparation of lanostane (Voser, Montavon, Günthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893; Barton, Bruun, Thomas, and Fawcett, *J.*, 1951, 3154), failed to effect the removal of oxygen from zeorininone. Instead, the vigorous Clemmensen conditions caused partial isomerisation to a further isomer, *neo*zeorininone, m. p. 238—240°, $[\alpha]_D$ −2°, in which the double bond and keto-group had *not* moved into conjugation.



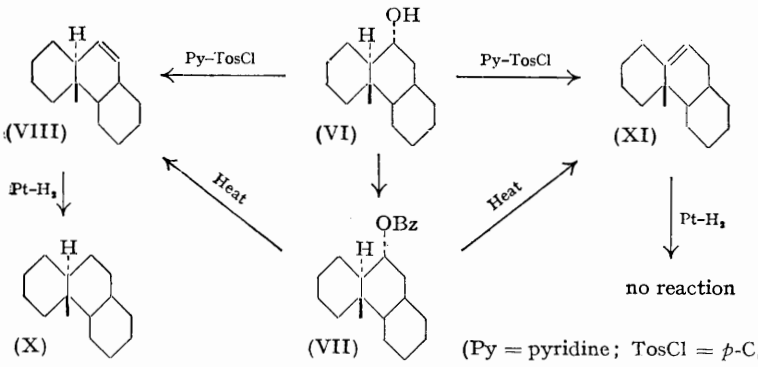
(I) (II) (III) (IV) (V)

The ready acylation of zeorin, zeorinin, *iso*zeorinin, and deoxyzeorin, combined with the high degree of steric hindrance of the corresponding carbonyl compounds, must be explained, on the basis of a six-membered ring (see above), by the hydroxyl group of zeorin being equatorial (Barton, *Experientia*, 1950, **6**, 316; Barton and Rosenfelder, *J.*, 1951, 1048). This was confirmed by lithium aluminium hydride reduction of deoxyzeorinone to *epi*deoxyzeorin (see footnote, p. 83, in the paper by Barton and Holness, *J.*, 1952, 78). The latter was smoothly oxidised back to deoxyzeorinone by chromic acid, but it resisted benzoylation under conditions adequate for the benzoylation of deoxyzeorin. Further confirmation came from the reduction of zeorininone to zeorinin by sodium and alcohol (see Barton, *loc. cit.*).

At this stage of the investigation it seemed clear that there might be a parallel between the chemistry of zeorin ($[\alpha]_D$ +54°), *iso*zeorinin ($[\alpha]_D$ +78°), and zeorinin ($[\alpha]_D$ +59°) on the one hand and of ψ-taraxastanediol (Morice and Simpson, *J.*, 1941, 181), taraxasterol ($[\alpha]_D$ +91°) (*e.g.*, Lardelli and Jeger, *Helv. Chim. Acta*, 1948, **31**, 813), and ψ-taraxasterol (*hetero*lupeol) ($[\alpha]_D$ +47°) (Burrows and Simpson, *J.*, 1938, 2042) on the other. Thus the series (II), (III), and (IV) *might* have been adequate partial formulæ for the above-mentioned relations in both series of compounds. It thus became of primary importance to effect the conversion of zeorin into the fundamental saturated hydrocarbon, for this could conceivably have been identical with *hetero*lupane (V). As mentioned above, attempts at the direct removal of the secondary oxygen function (as a carbonyl group) proved abortive. After a number of experiments, zeorinane was eventually obtained in the following two ways. (*a*) Dehydration of deoxyzeorin by toluene-*p*-sulphonyl chloride in boiling pyridine gave a mixture of monoethylenic hydrocarbons, which were hydrogenated by using a platinum catalyst in acetic acid to a mixture of saturated and unsaturated hydrocarbons. After destruction of the unsaturated hydrocarbon by the procedure of Anderson and Nabenhauer (*J. Amer. Chem. Soc.*, 1924, **46**, 1957), the saturated zeorinane remained unattacked. (*b*) Pyrolysis of deoxyzeorin benzoate gave a mixture of mono-

ethylenic hydrocarbons which, on further treatment as under (*a*), also furnished zeorinane. The yield was superior in the former procedure. Zeorinane had m. p. 186·5—187·5°, $[\alpha]_D$ +12°, and closely resembled *hetero*lupane in properties (Jeger, Krüsi, and Ruzicka, *Helv. Chim. Acta*, 1947, **30**, 1048). A reference specimen of the latter hydrocarbon, prepared from taraxasterol by a known route (Lardelli and Jeger, *ibid.*, 1948, **31**, 813) had the same melting point and rotation. However, zeorinane was *not* identical with *hetero*lupane, for there was a pronounced melting point depression on admixture. Zeorinane would appear to be a new fundamental hydrocarbon of the triterpenoid series.

These indirect methods of formation of zeorinane can be plausibly interpreted in terms of the partial formulæ (VI) (for deoxyzeorin), (VII) (for deoxyzeorin benzoate), (VIII), (IX), and (X), the last representing zeorinane. There is analogy for the pyrolysis reaction in the behaviour of 7-benzoyloxy-groups in the cholestane series (Barton and Rosenfelder, *J.*, 1949, 2459).



In spite of the apparent similarity of reactions and rotations in the zeorin and ψ-taraxastanediol series of compounds (see above) there are at least two major chemical differences. First, ψ-taraxasteryl acetate is readily hydrogenated (Lardelli, Krüsi, Jeger, and Ruzicka, *ibid.*, p. 1159) whereas zeorinin acetate, in our hands at least, is resistant. Secondly, taraxasteryl acetate is readily isomerised by hydrochloric acid in acetic acid to lupenyl-I acetate * whereas, under the *same* conditions, *iso*zeorinin acetate is isomerised to zeorinin acetate, but not further.

The secondary and tertiary hydroxyl groups in zeorin are either not close to each other in the molecule, or else they are separated by fully substituted centres. Thus the double bond and carbonyl group of zeorininone do not move into conjugation on treatment with acid (see above), and the mixture of hydrocarbons obtained by dehydration of zeorinin with toluene-*p*-sulphonyl chloride in pyridine is not isomerised to a conjugated diene by hydrochloric–acetic acids.

Experimental

M. p.s are uncorrected. All rotations were taken in chloroform solution: the values recorded have been approximated to the nearest degree.

Ultra-violet absorption spectra were determined in absolute ethanol solution, with a Unicam Spectrophotometer, Model SP 500. They have not been corrected for instrument error in the far ultra-violet range (cf. Bladon, Henbest, and Woods, *Chem. and Ind.*, 1951, 867).

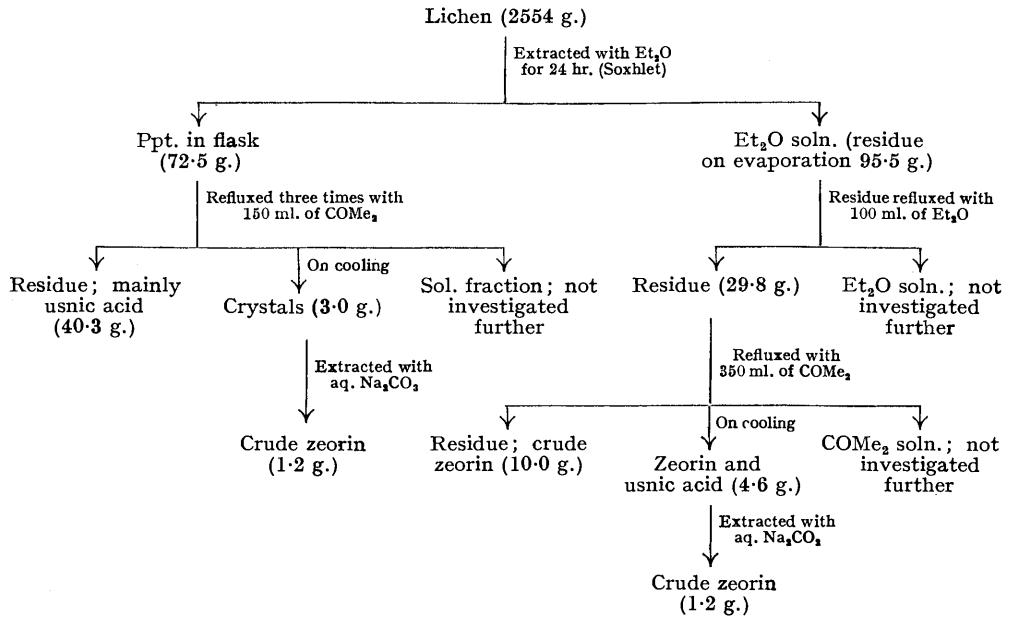
Infra-red absorption spectra were kindly determined by Dr. Hans Heymann (Harvard) and Dr. W. J. Rosenfelder (Harvard), using a Baird Associates (Cambridge, Mass.) recording double-beam instrument.

Alkaline hydrolyses were effected by using several equivalents of potassium hydroxide and refluxing for 30—60 minutes in methanolic or dioxan-methanolic solution depending on the solubility requirements of the ester.

Light petroleum refers throughout to the fraction of b. p. 40—60°.

* This reaction is under investigation by Professor E. R. H. Jones, F.R.S., Dr. T. G. Halsall, and their colleagues at the University of Manchester. It is our understanding that they will present a full report in due course.

Isolation of Zeorin.—Zeorin was obtained by extraction of *Nephroma arcticum* L. with ether according to the flow sheet below. The lichen had been collected by Professor and Mrs. N. A. Sörensen in the Oppdal district of Norway. It was freed from adhering mosses and earth, dried in air, and crushed in a porcelain ball-mill.



Purification of Zeorin.—Attempted fractionation of the crude zeorin by crystallisation from alcohol gave fractions with the following constants (in order of increasing solubility) : (i) m. p. 228—245°, $[\alpha]_D$ +48° (*c*, 0·54 in 2-dm. tube), (ii) m. p. 235—247°, $[\alpha]_D$ +53° (*c*, 0·50 in 2-dm. tube), (iii) m. p. 245—253°, $[\alpha]_D$ +54° (*c*, 0·47 in 4-dm. tube), (iv) m. p. 240—248°, $[\alpha]_D$ +55° (*c*, 0·52 in 2-dm. tube). In view of the widely different m. p.s recorded for zeorin in the literature (cf. Abderhalden's " Biochemisches Handlexikon," 1912, Vol. VII (1), p. 56 *et seq.*) and of the wide melting ranges found in our own experiments above, the homogeneity of zeorin was investigated. For this purpose chromatography of zeorin acetate was found convenient.

Crude zeorin (approx. 10 g.) was dissolved in dry pyridine, excess of acetic anhydride added, and the mixture left overnight at room temperature. Working up in the usual way afforded crude zeorin acetate. A small specimen, recrystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 223—230°, $[\alpha]_D$ +75° (*c*, 0·50 in 2-dm. tube). Alkaline hydrolysis gave back a zeorin of m. p. 220—233°, $[\alpha]_D$ +54° (*c*, 0·51 in 2-dm. tube). The bulk of the acetylated crude zeorin was chromatographed over alumina (29 fractions). Elution with 1 : 1 benzene–ether afforded pure zeorin acetate, m. p. 225—230° (unchanged on repeated crystallisation from chloroform–methanol), $[\alpha]_D$ +78° (*c*, 0·53 in 2-dm. tube), +78° (*c*, 0·52 in 2-dm. tube); the resolidified melt had the same m. p. range. It was concluded that, in spite of the wide m. p. range, the homogeneity of the zeorin acetate had been established (Found : C, 79·0; H, 11·05. Calc. for $C_{32}H_{54}O_3$: C, 78·95; H, 11·2%). A subsequent preparation of pure zeorin acetate also showed $[\alpha]_D$ +78° (*c*, 0·54 in 2-dm. tube).

Hydrolysis of zeorin acetate with refluxing 20% methanolic potassium hydroxide gave zeorin which, recrystallised from acetone, had m. p. 223—227°, $[\alpha]_D$ +54° (*c*, 0·50 in 2-dm. tube).

As a further confirmation of the homogeneity, 1 g. of zeorin was converted into the benzoate by being kept overnight in pyridine solution with excess of benzoyl chloride. Working up in the usual way and recrystallisation from benzene–acetone afforded *zeorin benzoate*, m. p. 236—246°, $[\alpha]_D$ +73° (*c*, 0·50 in 2-dm. tube) (Found : C, 80·7; H, 9·95. $C_{37}H_{56}O_3$ requires C, 80·95; H, 10·3%). Chromatography over alumina (30 fractions) demonstrated the homogeneity of the benzoate, $[\alpha]_D$ +75° (*c*, 0·51 in 2-dm. tube), after recrystallisation from acetone.

Zeorinone.—Zeorin (500 mg.) in " AnalaR " acetic acid (40 ml.) was treated with chromium

trioxide (100 mg.) in 0·1 ml. of water and 2 ml. of acetic acid at room temperature, and the solution set aside overnight. The reaction mixture was worked up in the usual way and the product recrystallised from chloroform–methanol, to give *zeorinone*, m. p. 239—245° (decomp.), $[\alpha]_D$ +35° (*c*, 0·57), $\lambda_{max.}$ 300 mμ ($\varepsilon_{max.}$ = 30) (Found: C, 81·2; H, 11·05. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%).

Zeorinin Acetate.—Zeorin acetate (1·0 g.) was treated with ethanol (132 ml.) and concentrated hydrochloric acid (26 ml.) according to the procedure of Asahina and Yosioka (*Ber.*, 1940, **73**, 742; cf. Zopf, *Annalen*, 1895, **288**, 50). Since the m. p. of the reaction product [m. p. 196—203°, $[\alpha]_D$ +71° (*c*, 0·54) after recrystallisation from chloroform–acetone] was not sharp it was deemed desirable to carry out a chromatographic fractionation (14 fractions) in order to establish its homogeneity. The m. p.s of the fractions ranged from 197—203° to 200—205°, the latter unchanged on repeated recrystallisation, whilst the rotations of the fractions were constant at approx. 70° (see below). It was concluded that, in spite of the wide m. p. range, the homogeneity of the zeorinin acetate had been established. The mean $[\alpha]_D$ based on seven determinations was +70°, $\lambda_{max.}$ 201 mμ ($\varepsilon_{max.}$ = 5500; ε_{215} = 1700) (*c*, 0·004) (Found: C, 81·8; H, 11·45. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%).

Treatment of zeorinin acetate in chloroform at room temperature for 15 minutes with gaseous dry hydrogen chloride, followed by removal of the solvent *in vacuo* and recrystallisation from chloroform–methanol, gave back zeorinin acetate, m. p. and mixed m. p. 200—203°, $[\alpha]_D$ +70° (*c*, 0·59).

Hydrolysis of zeorinin acetate as for zeorin acetate (see above) afforded zeorinin which, recrystallised from acetone–methanol, had m. p. 179—183°, $[\alpha]_D$ +59° (*c*, 0·50).

Asahina and Yosioka (*loc. cit.*) recorded m. p. 181—183°, $[\alpha]_D$ +50° for zeorinin and m. p. 197—200° for the acetate.

Zeorinin Benzoate.—Benzoylation of zeorinin with benzoyl chloride in pyridine overnight at room temperature and working up in the usual way furnished *zeorinin benzoate* which, recrystallised from chloroform–acetone, had m. p. 218—220°, $[\alpha]_D$ +51° (*c*, 0·59), +49° (*c*, 0·53), +50° (*c*, 0·51) (Found: C, 83·4; H, 10·15. $C_{37}H_{54}O_2$ requires C, 83·7; H, 10·25%).

Zeorininone.—*iso*Zeorininone (see below) (150 mg.) was treated with ethanolic hydrochloric acid as for the preparation of zeorinin acetate. Working up in the usual way and recrystallisation from chloroform–methanol furnished zeorininone, m. p. 173—176°. Further treatment in chloroform with hydrogen chloride furnished a more sharply melting preparation, m. p. 177—178°, $[\alpha]_D$ +21° (*c*, 0·50 in 2-dm. tube), $\lambda_{max.}$ 298 (ε = 50) and 200 mμ (ε = 8700; ε_{215} = 2700) (*c*, 0·0042) (Found: C, 84·35, 84·25; H, 11·1, 11·25. Calc. for $C_{30}H_{48}O$: C, 84·85; H, 11·4%). Oxidation of zeorinin by chromic acid at room temperature also afforded zeorininone, $[\alpha]_D$ +23° (*c*, 0·55), $\lambda_{max.}$ 299 mμ (ε = 50), but in very poor yield and only isolatable by careful chromatography. Zeorininone was recovered unchanged on attempted Wolff–Kishner reduction. For zeorininone Asahina and Yosioka (*loc. cit.*) recorded m. p. 184° but no rotation.

Zeorininone (100 mg.) was dissolved in 25 ml. of *n*-propanol and saturated with sodium at the reflux. After working up in the usual way the reaction product was acetylated with acetic anhydride–pyridine at room temperature for 24 hours. After the usual treatment the acetate was recrystallised from chloroform–methanol, to furnish somewhat impure zeorinin acetate, $[\alpha]_D$ +66° (*c*, 1·00), m. p. 190—195° undepressed on admixture with authentic material (see above).

Treatment of zeorininone with hydrochloric and acetic acids, as in the isomerisation of *iso*zeorinin acetate (see above), gave back starting material.

Zeorinin Acetate Oxide.—Zeorinin acetate (200 mg.) in " AnalaR " acetic acid (50 ml.) was heated on the steam-bath for 0·5 hour with addition of perhydrol (1 ml.). After working up in the usual way the reaction product was chromatographed over alumina, elution being with benzene and benzene to which 1% of ether had been added. All fractions melted at 255—258°. They were combined and recrystallised from chloroform–methanol, to give zeorinin acetate oxide, m. p. 255—257°, $[\alpha]_D$ +74° (*c*, 1·06) (Found: C, 78·8; H, 10·85. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). For this compound Asahina and Yosioka (*loc. cit.*) reported m. p. 255—257° also.

Zeorinin Benzoate Oxide.—Zeorinin benzoate (300 mg.) was treated with acetic acid and perhydrol as above. Recrystallisation of the product from chloroform–methanol gave *zeorinin benzoate oxide*, m. p. 259—260°, $[\alpha]_D$ +67° (*c*, 1·32), +66° (*c*, 1·07) (Found: C, 81·2; H, 9·8. $C_{37}H_{54}O_3$ requires, C, 81·25; H, 9·95%).

Dehydrozeorinin Benzoate.—Zeorinin benzoate oxide (200 mg.) was refluxed for two hours in 10 ml. of " AnalaR " acetic acid and 2 ml. of concentrated hydrochloric acid. After working

up in the usual way the product was filtered through alumina in benzene solution. The eluate was recrystallised from chloroform–methanol, to furnish *dehydrozeorinin benzoate*, m. p. 208—215° $[\alpha]_D$ +41° (*c*, 1·51), +40° (*c*, 1·19), +37° (*c*, 1·02), $\lambda_{max.}$ 235 and 252 mμ (ε = 20,000 and 18,000 respectively) (Found : C, 84·1; H, 10·25. $C_{37}H_{52}O_2$ requires C, 84·05; H, 9·9%). The m. p. was unchanged on repeated fractional crystallisation.

iso*Zeorinin Acetate*.—Zeorin acetate (500 mg.) was treated with phosphorus oxychloride (2 ml.) in pyridine (15 ml.) at room temperature overnight. After working up in the usual way the product was repeatedly recrystallised from chloroform–methanol, to give iso*zeorinin acetate*, m. p. 212—213°, $[\alpha]_D$ +108° (*c*, 0·54), +109° (*c*, 0·52) (Found : C, 81·65; H, 11·05. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). Further fractionation did not alter these constants.

Hydrolysis as for zeorin acetate (see above) gave iso*zeorinin* which, recrystallised from acetone, had m. p. 185—202°, $[\alpha]_D$ +78° (*c*, 0·50) (Found : C, 84·3; H, 11·95. $C_{30}H_{50}O$ requires C, 84·45; H, 11·8%). This with benzoyl chloride in pyridine at room temperature overnight gave, after working up in the usual way, iso*zeorinin benzoate*, m. p. 234—236°, $[\alpha]_D$ +100° (*c*, 0·52), from chloroform–methanol (Found : C, 83·05; H, 10·1. $C_{37}H_{54}O_2$ requires C, 83·7; H, 10·25%).

Treatment of *iso*zeorinin benzoate with ethanolic hydrochloric acid as in the preparation of zeorinin acetate (see above) afforded, in almost quantitative yield zeorinin benzoate, $[\alpha]_D$ +51° (*c*, 0·56), m. p. 219—220° undepressed on admixture with the authentic benzoate (see above).

To *iso*zeorinin acetate (400 mg.) in boiling acetic acid (10 ml.), concentrated hydrochloric acid (2 ml.) was added. The refluxing was continued for 30 minutes. Working up in the usual way and recrystallisation from chloroform–methanol gave zeorinin acetate, $[\alpha]_D$ +65° (*c*, 1·77), m. p. 195—198° undepressed on admixture with authentic material (see above). Under the same acid conditions taraxasteryl acetate was smoothly isomerised to lupenyl-I acetate.

iso*Zeorininone*.—Zeorinone (400 mg.) (see above) was treated with phosphorus oxychloride and pyridine as in the preparation of *iso*zeorinin acetate (see above). After working up in the usual way the product was repeatedly recrystallised from chloroform–methanol, to furnish iso*zeorininone*, m. p. 208—212°, $[\alpha]_D$ +31° (*c*, 0·56), +31° (*c*, 0·52), +30° (*c*, 0·50), $\lambda_{max.}$ 299 mμ (ε = 35) (Found : C, 84·5; H, 11·35. $C_{30}H_{48}O$ requires C, 84·85; H, 11·4%).

Deoxyzeorin Acetate.—(a) *Hydrogenation of* iso*zeorinin acetate*.—*iso*Zeorinin acetate (200 mg.) in anhydrous ether (25 ml.) and " AnalaR " acetic acid (75 ml.) was hydrogenated overnight with a platinum catalyst. After working up in the usual way, recrystallisation from chloroform–methanol furnished *deoxyzeorin acetate*, m. p. 202—203°, giving no colour with tetranitromethane (Found : C, 81·0; H, 11·4. $C_{32}H_{54}O_2$ requires C, 81·65; H, 11·55%).

Hydrolysis as for zeorin acetate (see above) gave *deoxyzeorin* which, recrystallised from chloroform–methanol, had m. p. 198—199° (Found : C, 82·6; H, 11·7. $C_{30}H_{52}O,\frac{1}{2}CH_3{\cdot}OH$ requires C, 82·35; H, 12·25%). Deoxyzeorin was further characterised by conversion into the benzoate by benzoyl chloride–pyridine overnight at room temperature. Working up in the usual way gave *deoxyzeorin benzoate*, m. p. 235—236° (from chloroform–methanol), $[\alpha]_D$ +56° (*c*, 0·59) (Found : C, 82·8; H, 10·4. $C_{37}H_{56}O_2$ requires C, 83·4; H, 10·6%).

(b) *Hydrogenation of zeorin acetate*. Zeorin acetate (1·02 g.) in anhydrous ether (50 ml.) and " AnalaR " acetic acid (75 ml.) was hydrogenated overnight with a platinum catalyst. Working up in the usual way gave deoxyzeorin acetate, m. p. 200—202° (from chloroform–methanol), $[\alpha]_D$ +51° (*c*, 1·46), undepressed in m. p. on admixture with the specimen prepared as above.

Hydrolysis and benzoylation as in (*a*) above furnished deoxyzeorin benzoate, $[\alpha]_D$ +51° (*c*, 2·14), m. p. 233—234° undepressed on admixture with the benzoate reported in (a) above.

Deoxyzeorinone.—Deoxyzeorin acetate (500 mg.) was hydrolysed as for zeorin acetate (see above) and the crude deoxyzeorin oxidised in " AnalaR " acetic acid (20 ml.) by addition of chromium trioxide (200 mg.) in water (0·5 ml.) and acetic acid (15 ml.). After being left overnight at room temperature the product was crystallised from chloroform–methanol, to give *deoxyzeorinone*, m. p. 199—200°, $[\alpha]_D$ −6° (*c*, 2·01 in 2-dm. tube), $\lambda_{max.}$ 299 mμ (ε = 40) (Found : C, 84·0; H, 11·75. $C_{30}H_{50}O$ requires C, 84·45; H, 11·8%). This ketone was also prepared by chromic acid oxidation of the deoxyzeorin from the hydrogenation of *iso*zeorinin acetate. It then had m. p. 200—201° and gave no depression in m. p. with the ketone prepared by the alternative route.

epi*Deoxyzeorin*.—Deoxyzeorinone (750 mg.) in dry ether (100 ml.) was reduced by refluxing with a large excess of lithium aluminium hydride for 1 hour. The reaction product, isolated after working up in the usual way, was benzoylated with pyridine–benzoyl chloride at room temperature. After the customary treatment the benzoylated product was dissolved in

3 : 1 benzene–light petroleum. A crystalline compound, m. p. 275—285° (decomp.), $[\alpha]_D$ +6° (*c*, 2·34), slowly separated. It was not investigated further, but was removed by filtration. Chromatography of the filtrate over alumina gave epi*deoxyzeorin*, eluted with 1 : 1 benzene–light petroleum and crystallised from chloroform–menthanol; it had m. p. 208—209°, $[\alpha]_D$ −9° (*c*, 2·04) (Found : C, 84·0; H, 12·15. $C_{30}H_{52}O$ requires C, 84·05; H, 12·2%). This compound was saturated to tetranitromethane and showed no selective absorption in the ultraviolet region, even at 195—215 mμ.

*epi*Deoxyzeorin (50 mg.) was oxidised by chromium trioxide as in the oxidation of deoxyzeorin (see above). The product, after recrystallisation from chloroform–methanol, afforded deoxyzeorinone, $[\alpha]_D$ −5° (*c*, 1·09), m. p. 199—200° undepressed on admixture with authentic material (see above) of the same m. p.

Zeorinane.—(a) *Dehydration of deoxyzeorin with toluene-*p*-sulphonyl chloride.* Deoxyzeorin (200 mg.) was heated under reflux for 8 hours with toluene-*p*-sulphonyl chloride (400 mg.) in pyridine (3 ml.). After working up in the usual way, the product was filtered through alumina in light petroleum solution. Recrystallisation from chloroform–methanol gave a mixture of monounsaturated hydrocarbons, m. p. 157—159°, $[\alpha]_D$ −4° (*c*, 1·02) $\lambda_{max.}$ 199 mμ (ε = 5000; ε_{215} = 800) (*c*, 0·004) (Found : C, 87·4; H, 12·1. Calc. for $C_{30}H_{50}$: C, 87·75; H, 12·25%). Further recrystallisation did not change the m. p. or rotation {$[\alpha]_D$ −4° (*c*, 1·01 in 2-dm. tube)}.

This hydrocarbon mixture (100 mg.) was hydrogenated in ether–acetic acid overnight. After working up in the usual way and crystallisation from chloroform–methanol a mixture of saturated and unsaturated hydrocarbons resulted, having m. p. 147—148°, which then resolidified and remelted at 167—168°, and had $[\alpha]_D$ +13° (*c*, 0·95), +14° (*c*, 1·06), $\lambda_{max.}$ 198 mμ (ε = 1900; ε_{215} = 300) (*c*, 0·0044) (Found : C, 87·5; H, 11·9%). The mixture gave only a faint colour with tetranitromethane.

(b) *Pyrolysis of deoxyzeorin benzoate.* Deoxyzeorin benzoate (200 mg.) was heated in a small flask at 350° (bath-temp.) for 5 minutes *in vacuo*. The pyrolysis product was filtered through alumina in light petroleum and recrystallised from chloroform–methanol. After each crystallisation the m. p. remained constant at 157—158°, but the rotation increased steadily {2 recrysts., $[\alpha]_D$ +6° (*c*, 1·08); 3 recrysts., $[\alpha]_D$ +10° (*c*, 1·15); 4 recrysts., $[\alpha]_D$ +13° (*c*, 1·03); 5 recrysts., $[\alpha]_D$ +14° (*c*, 1·13)}. The final material gave no depression in m. p. with the mixture of unsaturated hydrocarbons (m. p. 157—159°), prepared as under (a) above. It showed $\lambda_{max.}$ 198 mμ (ε = 3500; ε_{215} = 550) (*c*, 0·004) and gave a distinct colour with tetranitromethane.

Hydrogenation of this mixture of hydrocarbons as under (a) above furnished a mixture of unsaturated and saturated hydrocarbons which, recrystallised from chloroform–methanol, had m. p. 150—151°, then resolidified and remelted at 167—168°, $[\alpha]_D$ +14° (*c*, 1·12), +14° (*c*, 1·10), $\lambda_{max.}$ 198 mμ (ε = 3200; ε_{215} = 50) (*c*, 0·0048), unchanged on further recrystallisation. The mixed m. p. with the corresponding mixture of hydrocarbons reported under (a) was undepressed and showed the same double m. p. The mixture gave only a faint colour with tetranitromethane.

(c) *Isolation of zeorinane.* The mixtures of saturated and unsaturated hydrocarbons reported in (a) and (b) above were dissolved in carbon tetrachloride (5 ml.) and acetic anhydride (0·5 ml.). Concentrated sulphuric acid (0·4 ml.) was then added dropwise with cooling. A further 0·5 ml. of acetic anhydride was added and the mixture left at room temperature for 30 minutes. After working up in the usual way the product was filtered in light petroleum solution through alumina. Once recrystallised from chloroform–methanol, it melted at 176—182°, gave no colour with tetranitromethane or with the Liebermann–Burchard reagent, and showed no maximum in the 195—215 mμ region (ε <25).

This procedure was repeated on a larger scale (from 400 mg.) of deoxyzeorin, method (*a*) being used, and recrystallisation of the saturated hydrocarbon was continued until there was no further change in m. p. or rotation. This afforded *zeorinane*, m. p. 186·5—187·5°, $[\alpha]_D$ +12° (*c*, 1·00) (Found : C, 87·5; H, 12·6. $C_{30}H_{52}$ requires C, 87·3; H, 12·7%).

Dehydration of Zeorinin.—Zeorinin (100 mg.) was heated under reflux with toluene-*p*-sulphonyl chloride (200 mg.) in pyridine (3 ml.) for 9 hours. After working up in the usual way and filtration in light petroleum through alumina a hydrocarbon mixture was obtained which, recrystallised from chloroform–methanol, melted constantly at 150—151° and had $[\alpha]_D$ +55° (*c*, 1·15), +56° (*c*, 1·03) (Found : C, 88·1; H, 12·2. Calc. for $C_{30}H_{48}$: C, 88·15; H, 11·85%).

The mixture (50 mg.) was refluxed with " AnalaR " acetic acid (70 ml.) and concentrated hydrochloric acid (20 ml.) for 32 hours. Examination of the 215—300-mμ region gave no indication of selective butadienyl-type absorption in the crude reaction product.

Rearrangement of Zeorininone.—Zeorininone (400 mg.) was heated under reflux with dioxan (10 ml.) and concentrated hydrochloric acid (8 ml.) for 72 hours. After working up in the usual way, the product was crystallised repeatedly from chloroform–methanol, to give the highly crystalline neo*zeorininone*, m. p. 238—240°, $[\alpha]_D$ −2° (*c*, 1·05), −3° (*c*, 1·03), unchanged on further recrystallisation. This compound showed no high-intensity selective absorption in the 215—280-mμ region. It was not possible to detect the low-intensity saturated-ketone band in the 290-mμ region because of the sparing solubility of the ketone in ethanol. However, it showed $\lambda_{max.}$ 201 mμ (ε = 9100; ε_{215} = 4900) (*c*, 0·004) (Found: C, 84·0, 83·9; H, 11·1, 11·35. $C_{30}H_{48}O$ requires C, 84·85; H, 11·4%). *neo*Zeorininone was also obtained from an attempted Clemmensen reduction of zeorininone under the same conditions of acidity and reflux time (see Barton, Bruun, Fawcett, and Thomas, *J.*, 1951, 3154).

Preparation of hetero*Lupane.*—Taraxasterol was extracted from chamomile flowers by following the general directions of Burrows and Simpson (*J.*, 1938, 2042), except that it was found advantageous to use ether instead of carbon tetrachloride for the extraction. The crude taraxasterol was converted into the acetate and purified by chromatography over alumina. The acetate, recrystallised from chloroform–methanol, had m. p. 245—247°, $[\alpha]_D$ +100° (*c*, 1·37). The ester was hydrogenated in ether–acetic acid, to give taraxastanyl acetate which, recrystallised from chloroform–methanol, had m. p. 262—263°, $[\alpha]_D$ +16° (*c*, 2·06). For the latter compound Lardelli and Jeger (*Helv. Chim. Acta*, 1948, **31**, 813) recorded $[\alpha]_D$ +23°, but later the value of +19° was given (Lardelli, Krüsi, Jeger, and Ruzicka, *ibid.*, p. 1159). Alkaline hydrolysis of taraxastanyl acetate followed by chromic acid oxidation afforded taraxastanone which, recrystallised from chloroform–methanol, had m. p. 171—172°, $[\alpha]_D$ +42° (*c*, 2·77) (Lardelli and Jeger, *loc. cit.*, recorded $[\alpha]_D$ +45°). Wolff–Kishner reduction of the ketone and chromatography over alumina (elution with light petroleum) furnished *hetero*lupane which, recrystallised from chloroform–methanol, had m. p. 186—188°, $[\alpha]_D$ +11° (*c*, 2·17) (Found: C, 87·4; H, 12·5. Calc. for $C_{30}H_{52}$: C, 87·3; H, 12·7%). *hetero*Lupane gave a 30° m. p. depression on admixture with zeorinane (see above). *hetero*Lupane was recovered unchanged after treatment with acetic anhydride–sulphuric acid as in the Anderson–Nabenhauer procedure (see above).

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