429. *The Constitution of the Neutral, Tetracyclic Triterpenes of Dammar Resin.*

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The main constitutional features of the neutral, tetracyclic triterpenes of dammar resin have been elucidated. Dammarenediols I and II contain a 3β-hydroxyl group, a tertiary hydroxyl group, and a single double bond present in an *iso*propylidene group. Dehydration of their 3-acetates yielded dammaradienyl acetate, which contains a vinylidene group, together with an isomer. Acid-catalysed dehydration of the dihydro-derivative of dammarenediol II monoacetate yielded the known compounds *iso*tirucallenyl acetate (XI; R = Ac) and *iso*euphenyl acetate (X; R = Ac). This established the main carbon skeleton and confirmed the location of the tertiary hydroxyl group at $C_{(20)}$. The I and II isomers have been shown to differ only in their configuration at $C_{(20)}$ by converting them both into the same 20-oxo-compounds. On the basis of these experiments dammarenediol I and II are formulated as (I; R = OH) and dammaradienol as (III; R = OH).

The isolation of a number of neutral, tetracyclic triterpenes from dammar resin was described recently.[1] These comprise the diethenoid alcohol dammaradienol and its related ketone dammaradienone, together with the two monoethenoid diols, dammarenediol I and II and their related ketols hydroxydammarenone I and II. Experiments reported earlier and in the present paper allow formula (I; R = OH) to be advanced for both diols, (II) for both ketols, (III; R = OH) for dammaradienol, and (IV) for dammaradienone. A preliminary account to this effect has already appeared.[2] Two groups of workers [3,4] have pointed out the probable identity of hydroxydammarenone II with dipterocarpol,[5] and have also isolated this compound from the balsams and heartwoods of several *Dipterocarpus* species.

The earlier experiments revealed the simple relation between the two diols and the two ketols, and their tetracyclic nature. Oxidation of the hydroxydammarenones with chromic acid yielded trisnor-γ-lactones of probable partial formula (VI) together with acetone. The reactive double bond was thus present in an *iso*propylidene group, and the hydroxyl group common to both the ketols and diols was probably tertiary and located at $C_{(20)}$ as in (VII). The saturated nature of these lactones indicated a striking difference from the typical tetracyclic triterpenes euphol, tirucallol, and lanosterol [6] (all V; R = OH) in the absence of a nuclear double bond. This observation has now been confirmed by the

[1] Mills and Werner, *J.*, 1955, 3132.
[2] Mills, *Chem. and Ind.*, 1956, 189.
[3] Cosserat, Ourisson, and Takahashi, *ibid.*, p. 190.
[4] Godson, King, and King, *ibid.*, p. 190.
[5] van Itallie, *Arch. Pharm.*, 1912, **250**, 204.
[6] For reviews see Halsall and Jones, *Fortschr. Chem. org. Naturstoffe*, 1955, **12**, 44; Gascoigne and Simes, *Quart. Rev.*, 1955, **9**, 328.

preparation of a number of dihydro-derivatives, all saturated to tetranitromethane. It was also demonstrated earlier that no *cyclo*propane ring, such as occurs in *cyclo*artenol,[7] was present.

Dammaradienol was known to be tetracyclic and to have one of its two double bonds present in a vinylidene group. It was thus possibly the dehydration product of one or both dammarenediols in view of the probable location of the tertiary hydroxyl group in the latter at a position α to a methyl group. In fact, dehydration of both diol monoacetates with phosphorus oxychloride in pyridine yielded identical mixtures of double-bond isomers, in which the presence of dammaradienyl acetate was demonstrated. Thus partial formulæ (VII) and (VIII) for the diols and dammaradienol respectively mutually support one another. The remaining part of the mixture was probably the isomer (IX) (see below).

These compounds were directly correlated with other tetracyclic triterpenes by acid-catalysed dehydration of dammaranediol II monoacetate under the conditions used by Christen *et al.* for isomerisation of euphenyl acetate.[8] This yielded *iso*tirucallenyl acetate [9,10] (XI; R = Ac) and *iso*euphenyl acetate [8,11–14] (X; R = Ac) in about equal amounts. These two compounds differ only in their configuration at $C_{(20)}$ and consequently the formation of both of them here must proceed *via* the carbonium ion (XII): the tertiary hydroxyl group must therefore be at $C_{(20)}$. Further the isomerisation of the primary dehydration product to the isomers (X and XI; R = Ac) must be a simple rearrangement and cannot involve migration of methyl groups as in the formation of these compounds from tirucallenyl and euphenyl acetate. It follows that dammarenediol II must be represented by (I; R = OH) and that dammaradienol is (III; R = OH).

Dehydration of dammaranediol II monoacetate with phosphorus oxychloride in pyridine gave a mixture of double-bond isomers analogous to that given by dammarenediol II monoacetate. Ozonolysis of this mixture yielded, as volatile products, formaldehyde and *iso*hexanal but no 6-methylheptan-2-one, indicating the presence in the mixture of the isomers (XIII) and (XIV) but the absence of (XV). The non-volatile products were 3β-acetoxynordammaran-20-one (XVI) and 3β-acetoxyhexakisnordammaran-20-one (XVII) which each showed the expected infrared band at 1706 cm.$^{-1}$ (side-chain ketone). Several reduction products of these compounds have been prepared by standard procedures.

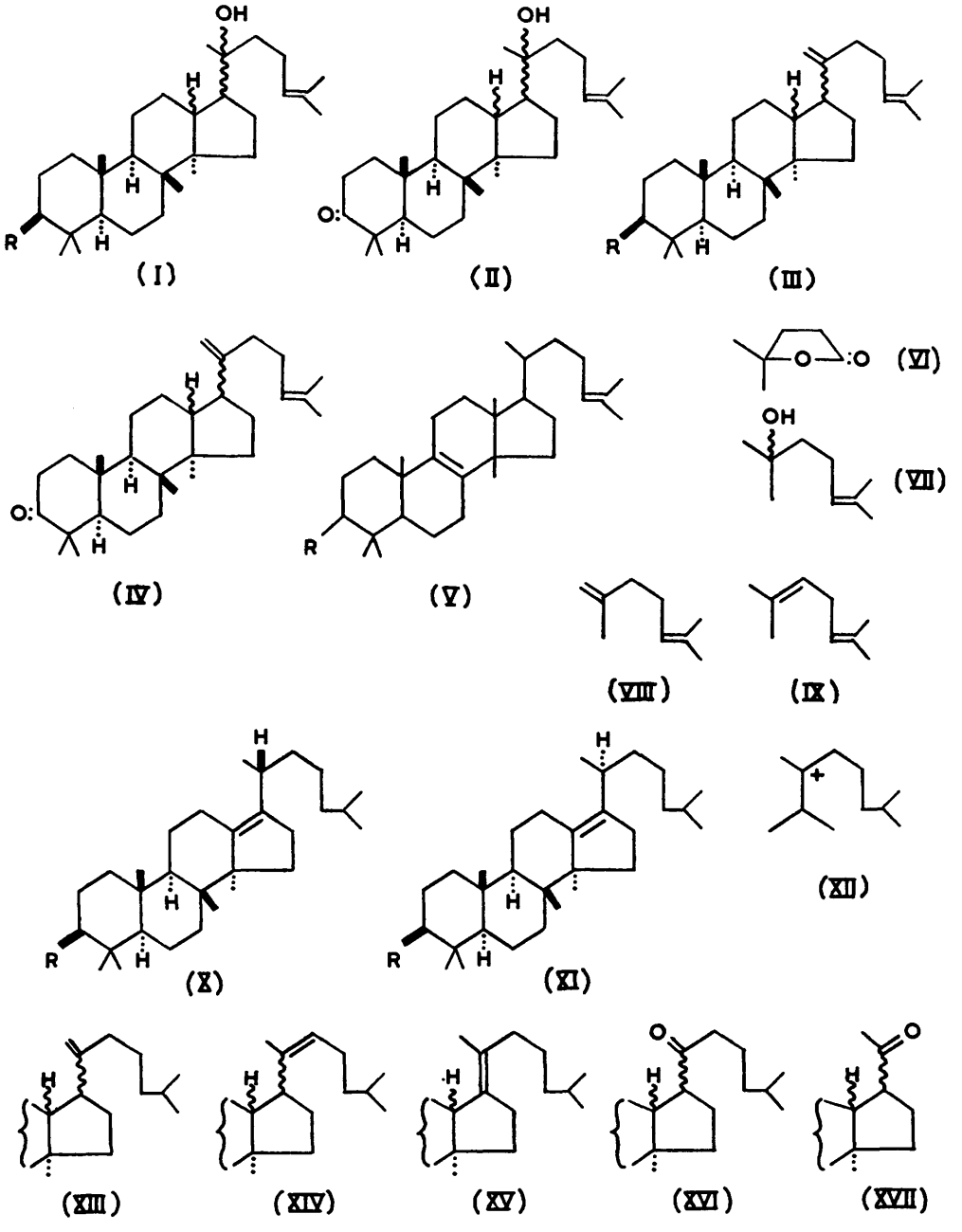
Direct oxidation of dammaranediol II monoacetate with chromium trioxide in acetic acid gave, in rather poor yield, the same two compounds (XVI) and (XVII) as were obtained by ozonolysis of its dehydration products. Oxidation of dammaranediol I monoacetate gave the same result. In these compounds the asymmetry at $C_{(20)}$ is destroyed while the original configuration in the rest of the molecule is preserved, and it follows that the I and II isomers differ only in their configuration at $C_{(20)}$. This conclusion follows also from the formation of identical mixtures on dehydration of the two diol monoacetates. In contrast to the oxidation of the anediol monoacetates, oxidation of the enediol monoacetates gave the expected lactones (VI).

Hydrogenation of dammaradienyl acetate yielded a mixture of saturated stereoisomeric acetates, resolved with some difficulty into dammaranyl A acetate and dammaranyl B acetate, which presumably differ in their configuration at $C_{(20)}$. The melting points of the two acetates were close and were not depressed on admixture. A depression of melting point was however observed on admixture of the two corresponding alcohols.

The stereochemistry of these compounds may now be considered. The configurations at positions 5, 10, 8, 9, and 14 must be the same as in *iso*euphenol and *iso*tirucallenol, and correspond to a *trans-anti-trans*-fusion of rings A, B, and C. There remains to be defined the configuration of the 13-hydrogen atom, the 17-side chain, and position 20. Ruzicka and his colleagues [15] have shown how the formulæ of typical members of all the main groups

[7] Barton, *J.*, 1951, 1444.
[8] Christen, Dünnenberger, Roth, Heusser, and Jeger, *Helv. Chim. Acta*, 1952, **35**, 1756.
[9] Arigoni, Jeger, and Ruzicka, *ibid.*, 1955, **38**, 222.
[10] Barbour, Lourens, Warren, and Watling, *J.*, 1955, 2194.
[11] Vilkas, *Bull. Soc. chim. France*, 1950, 582, and earlier papers.
[12] Dawson, Halsall, and Swayne, *J.*, 1953, 590.
[13] Barton, McGhie, Pradhan, and Knight, *Chem. and Ind.*, 1954, 1325; *J.*, 1955, 876.
[14] Arigoni, Viterbo, Dünnenberger, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1954, **37**, 2306.
[15] Arigoni, Eschenmoser, Jeger, and Ruzicka, *ibid.*, 1955, **38**, 1890.

of tetra- and penta-cyclic triterpenes may be derived from that of squalene in their full constitutional and configurational detail. According to their mechanism of triterpene biogenesis a fully *trans-anti-trans-anti-trans*-fusion of rings A—D is in the dammarenediols



and accordingly the 13-hydrogen atom would be β-situated. This has not yet been confirmed chemically but will be assumed for convenience in the following discussion.

It was suggested earlier [2] that the non-formation of a 17 : 20-double bond on dehydration of dammaranediol II monoacetate indicated an α(axial)-side chain. In this configuration the hydroxyl group might not be able to adopt a position favourable for elimination with

the 17-hydrogen atom owing to the interaction of the 14-methyl group with the methyl or methylene groups attached to $C_{(20)}$. An analogous explanation has been advanced by Fieser and Fieser [16] for the non-formation of a 17 : 20-double bond on dehydration of 20-methyl*allo*pregnane-3β : 20-diol,[17] and by Warren and his colleagues [10] for the same result on elimination of phenylthiourea form the appropriate elemi acid derivative.[18,19] On the other hand, apart from hydrolysis of the acetate group, both 3β-acetoxynordammaran-20-one and 3β-acetoxyhexakisnordammaran-20-one are stable to drastic treatment with alkali, which indicates that the side chain is in the more stable β(equatorial)-configuration, a conclusion supported by biogenetic considerations. Various possible molecular-rotation correlations do not lead to a decisive result and so will not be presented here. Again it would be unjustifiable to assign configurations at $C_{(20)}$ in the I and II isomers and in dammaranol A and dammaranol B in view of the unexplained anomalies in the molecular-rotation data for euphol and tirucallol: the signs of the molecular-rotation differences between derivatives of euphol and of tirucallol are opposite to those between derivatives in the *iso*-series (cf. ref. 10), though in both cases the only structural difference lies in the configuration at $C_{(20)}$.

Experimental

Rotations were determined in $CHCl_3$. Alumina for chromatography was Peter Spence's neutral type " H ", partially deactivated by exposure to the air. Light petroleum refers to the fraction of b. p. 60—80°.

Benzoates.—Benzoylation with pyridine–benzoyl chloride at room temperature overnight, followed by chromatography and crystallisation from ethanol, yielded *dammarenediol I monobenzoate* (I; R = Bz) as needles, m. p. 166—168°, $[\alpha]_D$ +54° (*c* 0·88) (Found: C, 80·3; H, 10·45. $C_{37}H_{56}O_3$ requires C, 80·95; H, 10·3%). Similarly dammarenediol II yielded its *monobenzoate* as needles (from ethanol), m. p. 156—158°, $[\alpha]_D$ +59° (*c* 0·92) (Found: C, 80·7; H, 10·55%). Benzoylation of dammaradienol gave *dammaradienyl benzoate* (III; R = Bz) which however, even after chromatography, separated from ethanol as an amorphous solid, m. p. 127—130°, $[\alpha]_D$ +70° (*c* 1·01) (Found: C, 83·0; H, 10·4. $C_{37}H_{54}O_2$ requires C, 83·7; H, 10·3%).

Dehydration of Dammarenediol I and II Monoacetates.—Dammarenediol II monoacetate (1·5 g.) in pyridine (20 ml.) was treated with phosphorus oxychloride (3 ml.) for 1 hr. at 20°. Dilution with water gave crystals which were adsorbed from light petroleum on alumina (15 × 1·8 cm.). Elution with benzene–light petroleum (1 : 9) gave a mixture of double-bond isomers, which after two crystallisations from ethanol had constant m. p. 146—150°, raised to m. p. 148—152° on admixture with dammaradienyl acetate (m. p. 151—153°), $[\alpha]_D$ +48° (*c* 1·76) (Found: C, 81·75; H, 11·25. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). Dammarenediol I monoacetate gave a similar mixture of isomers, m. p. and mixed m. p. 146—150°, $[\alpha]_D$ +48° (*c* 0·89). The infrared spectra of these mixtures showed bands at 3070, 1640, and 895 cm.$^{-1}$. The m. p.s fell to *ca.* 115—145° in a few weeks. The mixed acetates (300 mg.) in glacial acetic acid (15 ml.) and benzene (2 ml.) were treated with chromium trioxide (250 mg.) and set aside for 4 hr. at 20°. The products, isolated with ether, were adsorbed from light petroleum on alumina. Elution with benzene–light petroleum (1 : 9) and crystallisation from ethanol gave dammaradienyl acetate (30 mg.), m. p. and mixed m. p. 150—152°, $[\alpha]_D$ +62° (*c* 0·6) (Found: C, 81·5; H, 11·2%).

Hydrogenation Products.—Hydrogenation of dammarenediol I and II, and their monoacetates, and of hydroxydammarenone I and II in ethanol–ethyl acetate in the presence of Adams catalyst yielded the following products, none of which gave a colour with tetranitromethane: *Dammaranediol I*, m. p. 156—158°, $[\alpha]_D$ +30° (*c* 0·99) (Found: C, 80·2; H, 12·2. $C_{30}H_{54}O_2$ requires C, 80·65; H, 12·2%). *Dammaranediol II*, m. p. 133—135°, $[\alpha]_D$ +35° (*c* 0·93) (Found: C, 81·0; H, 12·2%). *Dammaranediol I monoacetate*, m. p. 145—147°, $[\alpha]_D$ +40° (*c* 0·77) (Found: C, 78·9; H, 11·65. $C_{32}H_{56}O_3$ requires C, 78·55; H, 11·95%). *Dammaranediol II monoacetate*, m. p. 106—108°, $[\alpha]_D$ +41° (*c* 0·82) (Found: C, 78·0; H, 11·55%). *Hydroxydammaranone I*, m. p. 154—156°, $[\alpha]_D$ +63° (*c* 0·42) (Found: C, 80·75; H, 12·0. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%). *Hydroxydammaranone II*, m. p. 95—105° (with

[16] Fieser and Fieser, *Experientia*, 1948, **4**, 286.
[17] Koechlin and Reichstein, *Helv. Chim. Acta*, 1944, **27**, 549.
[18] Arnold, Koller, and Jeger, *ibid.*, 1951, **34**, 555.
[19] Mazur, Koller, Jeger, and Ruzicka, *ibid.*, 1952, **35**, 181.

evolution of solvent), $[\alpha]_D$ +66° (*c* 0·59) (Found: C, 79·3; H, 11·85. $C_{31}H_{52}O_2,\frac{1}{2}CH_3{\cdot}OH$ requires C, 79·45; H, 11·85%).

Acid-catalysed Dehydration of Dammaranediol II Monoacetate.—A solution of the acetate (2·2 g.) in glacial acetic acid (60 ml.) containing sulphuric acid (2N; 2 ml.) was refluxed for 2 hr. The product was isolated with ether, adsorbed from light petroleum on alumina (26 × 3·8 cm.), and eluted with the same solvent (30 × 100 ml.). Fractions 8—11 yielded *iso*tirucallenyl acetate (XI; R = Ac) (from methanol) (480 mg.), m. p. and mixed m. p. 95—96·5°, $[\alpha]_D$ 0° (*c* 0·75) (Found: C, 81·3; H, 11·6. Calc. for $C_{32}H_{54}O_2$: C, 81·65; H, 11·55%). Fractions 12—15 yielded mixtures of wide m. p. Fractions 16—30 yielded *iso*euphenyl acetate (X; R = Ac) (from methanol) (515 mg.), m. p. and mixed m. p. 111—113°, $[\alpha]_D$ +8° (*c* 0·94) (Found: C, 81·3; H, 11·65%). Hydrolysis of *iso*tirucallenyl acetate with 10% ethanolic potassium hydroxide for 48 hr. at 20° gave *isotirucallenol* as needles (from methanol), m. p. 146—148°, $[\alpha]_D$ +7° (*c* 0·68) (Found: C, 83·65; H, 12·3. $C_{30}H_{52}O$ requires C, 84·0; H, 12·25%). Similar hydrolysis of *iso*euphenyl acetate gave *iso*euphenol, m. p. *ca.* 100°, $[\alpha]_D$ +19° (*c* 0·98).

Mixed Dammarenyl Acetates and their Ozonolysis Products.—Dammaranediol II monoacetate (3·8 g.) in pyridine (40 ml.) was treated with phosphorus oxychloride (8 ml.) for 1 hr. at room temperature. Dilution with water gave a solid which was filtered through alumina in benzene–light petroleum (1 : 9) and crystallised once from ethanol, to give a mixture of isomeric dammarenyl acetates, m. p. 137—146°, $[\alpha]_D$ +39° (*c* 0·94). The mixed acetates (3 g.) in glacial acetic acid (200 ml.) were treated with ozonised oxygen until the solution gave no colour with tetranitromethane (4 hr.). The solution was poured into water and steam-distilled, and the distillate (250 ml.) passed into a solution of dimedone in aqueous methanol which was then concentrated. Crystals (70 mg.) separated, identified after recrystallisation as the formaldehyde–dimedone compound by m. p. and mixed m. p. (189°). The distillate was treated with a solution of 2 : 4-dinitrophenylhydrazine in dilute hydrochloric acid and the derivative which separated was chromatographed in benzene on alumina (20 × 3·8 cm.). Development and elution with benzene gave only one band which yielded crystals (430 mg.), m. p. 97° (from aqueous methanol), of *iso*hexanal 2 : 4-dinitrophenylhydrazone, raised to m. p. 99—100° on recrystallising from light petroleum (Brunner and Farmer [20] give m. p. 99°) (Found: C, 51·5; H, 5·95; N, 20·8. Calc. for $C_{12}H_{16}O_4N_4$: C, 51·4; H, 5·75; N, 20·0%). The residue from the steam-distillation (2·6 g.) showed on a paper chromatogram (cf. ref. 1) two spots, of R_F 0·29 and 0·68, and a mauve Noller and a negative Halphen–Hicks colour reaction. It was adsorbed on alumina (35 × 3·8 cm.) from benzene–light petroleum (1 : 3) and eluted with the same solvent (1·3 l.) followed by benzene–light petroleum (1 : 1; 2·5 l.) and benzene (800 ml.) in 46 × 100 ml. fractions. Fractions 16—20 yielded 3β-*acetoxynordammaran*-20-*one* (XVI) (600 mg.), as needles, m. p. 164—165° (from methanol), $[\alpha]_D$ +66° (*c* 0·68) (Found: C, 78·45; H, 11·15. $C_{31}H_{52}O_3$ requires C, 78·7; H, 11·1%), R_F 0·29. Fractions 21—26 gave mixtures (800 mg.). Fractions 27—45 yielded 3β-*acetoxyhexakisnordammaran*-20-*one* (XVII) (750 mg.) as needles, m. p. 204—205° (from methanol), $[\alpha]_D$ +67° (*c* 1·12) (Found: C, 77·45; H, 10·65. $C_{26}H_{42}O_3$ requires C, 77·55; H, 10·55%), R_F 0·68. Hydrolysis of 3β-acetoxynordammaran-20-one with 10% ethanolic potassium hydroxide for 2 hr. on the steam-bath gave a product which did not crystallise well. On reacetylation however this material gave back the original acetate, identified by m. p. and mixed m. p. Similar hydrolysis of 3β-acetoxyhexakisnordammaran-20-one for 2 or for 20 hr. yielded, after chromatography and crystallisation from aqueous methanol, 3β-*hydroxyhexakisnordammaran*-20-*one*, m. p. 194—195°, $[\alpha]_D$ +55° (*c* 1·02) (Found: C, 79·55; H, 11·25. $C_{24}H_{40}O_2$ requires C, 79·9; H, 11·2%). Reacetylation of this compound gave back the orginal acetate (m. p. and mixed m. p.).

Nordammarane-3β : 20-*diol.*—3β-Acetoxynordammaran-20-one (150 mg.) in propan-2-ol (40 ml.) was treated with sodium (3 g.) during 1½ hr. on the steam-bath. The product was isolated with ether and adsorbed from benzene on alumina. Elution with ether–benzene (1 : 4) and crystallisation from nitromethane gave *nordammarane*-3β : 20-*diol* as needles, m. p. 165—167°, $[\alpha]_D$ +44° (*c* 0·86) (Found: C, 80·75; H, 12·15. $C_{29}H_{52}O_2$ requires C, 80·5; H, 12·15%). The diacetate was a gum.

Hexakisnordammarane-3β : 20-*diol.*—3β-Acetoxyhexakisnordammaran-20-one was reduced with sodium, chromatographed, and crystallised as described in the preceding section, to give *hexakisnordammarane*-3β : 20-*diol* as needles, m. p. 183° after extensive sintering, $[\alpha]_D$ +44° (*c* 0·86) (Found: C, 78·1; H, 11·7. $C_{24}H_{42}O_2,\frac{1}{2}CH_3{\cdot}OH$ requires C, 77·7; H, 11·75%). The *diacetate*, after chromatography and crystallisation from methanol, had m. p. 151°, then

[20] Brunner and Farmer, *J.*, 1937, 1039.

resolidifying and remelting at 160°, $[\alpha]_D$ +47° (*c* 1·03) (Found: C, 75·5; H, 10·5. $C_{28}H_{46}O_4$ requires C, 75·3; H, 10·2%).

Nordammaranyl Acetate.—3β-Acetoxynordammaran-20-one (200 mg.) in ethylene glycol (8 ml.) was heated with 85% hydrazine hydrate (0·5 ml.) under reflux for 1 hr. A solution of sodium (0·4 g.) in ethylene glycol (8 ml.) was then added, the water and excess of hydrazine were distilled off, and the residue was refluxed for 5 hr. The product was isolated with ether and treated with pyridine–acetic anhydride on the steam-bath. The solvents were removed *in vacuo*, and the residue was filtered in benzene–light petroleum (1 : 9) through alumina and crystallised from methanol, to give *nordammaranyl acetate* as plates (70 mg.), m. p. 109—111°, $[\alpha]_D$ +66° (*c* 0·97) (Found: C, 80·6; H, 11·85. $C_{31}H_{54}O_2$ requires C, 81·1; H, 11·9%).

Hexakisnordammaranyl Acetate.—3β-Acetoxyhexakisnordammaran-20-one (100 mg.) was reduced by the modified Wolff–Kishner procedure, as in the preceding section, and the product acetylated and chromatographed, to give *hexakisnordammaranyl acetate* as needles, m. p. 162—163° (from ethanol), $[\alpha]_D$ +66° (*c* 1·09) (Found: C, 80·25; H, 11·5. $C_{26}H_{44}O_2$ requires C, 80·35; H, 11·45%).

Oxidation of Dammaranediol I Monoacetate.—The acetate (359 mg.) in glacial acetic acid (15 ml.) was treated with chromium trioxide (400 mg.) in a few drops of water, and the solution kept overnight at 40°. The products, isolated with ether, were adsorbed on alumina (17 × 1·8 cm.) and eluted with benzene–light petroleum (1 : 1) (13 × 100 ml.). Fractions 4 and 5 yielded 3β-acetoxynordammaran-20-one, m. p. and mixed m. p. 163—165° (from methanol) (45 mg.), $[\alpha]_D$ +62° (*c* 0·45). Fractions 8—10, crystallised three times from methanol, yielded 3β-acetoxyhexakisnordammaran-20-one (20 mg.), m. p. and mixed m. p. 202—204°.

Oxidation of Dammaranediol II Monoacetate.—Dammaranediol II monoacetate, oxidised and chromatographed as in the preceding section, also yielded 3β-acetoxynordammaran-20-one, m. p. and mixed m. p. 163—165°, and 3β-acetoxyhexakisnordammaran-20-one, m. p. and mixed m. p. 203—205°, $[\alpha]_D$ +66° (*c* 0·64).

Oxidation of Dammarendiol I Monoacetate.—The acetate (200 mg.) in glacial acetic acid (20 ml.) and benzene (2 ml.) was treated with chromium trioxide (200 mg.) at room temperature overnight. Isolation with ether and crystallisation from ethanol–ethyl acetate gave 3β-*acetoxy*-20-*hydroxytrisnordammaranoic* 24→20-*lactone I* (*acetoxy-lactone I*) as plates, m. p. 278—279°, $[\alpha]_D$ +28° (*c* 1·08) (Found: C, 75·5; H, 10·2. $C_{29}H_{46}O_4$ requires C, 75·9; H, 10·15%).

Oxidation of Dammarenediol II Monoacetate.—Oxidation of dammarenediol II monoacetate with chromium trioxide as in the preceding section yielded 3β-*acetoxy*-20-*hydroxytrisnordammaranoic* 24→20-*lactone II* (*acetoxy-lactone II*) as prisms, m. p. 249—250°, $[\alpha]_D$ +49° (*c* 1·52) (Found: C, 76·05; H, 10·25%).

Hydrogenation of Dammaradienyl Acetate.—The acetate (1·15 g.) in ethanol–ethyl acetate (1 : 1; 50 ml.) was hydrogenated over Adams catalyst (50 mg.) for 1 hr. Filtration and removal of the solvent *in vacuo* gave crystals, m. p. 132—137°, which were adsorbed from light petroleum on alumina (35 × 3·8 cm.) and eluted with the same solvent (36 × 100 ml.). Fractions 13—16 yielded material (300 mg.), m. p. 139—141° (from ethanol), which was rechromatographed on alumina, the earlier fractions yielding *dammaranyl A acetate* as plates, m. p. 141—142° (from ethanol), $[\alpha]_D$ +45° (*c* 0·89) (Found: C, 81·35; H, 12·1. $C_{32}H_{56}O_2$ requires C, 81·25; H, 11·95%). Fractions 20—31 yielded materials (400 mg.) of m. p. *ca.* 132—135° (from ethanol) which were rechromatographed on alumina, the later fractions yielding *dammaranyl B acetate* as plates, m. p. 134—135° (from ethanol), mixed m. p. with dammaranyl A acetate 136—140°, $[\alpha]_D$ +61° (*c* 0·76) (Found: C, 81·05; H, 12·05%). Hydrolysis of dammaranyl A acetate for 48 hr. at 20° with 10% ethanolic potassium hydroxide, chromatographic purification of the product, and crystallisation from nitromethane gave *dammaranol A* as needles, m. p. 126—127°, $[\alpha]_D$ +36° (*c* 0·9) (Found: C, 84·0; H, 12·8. $C_{30}H_{54}O$ requires C, 83·6; H, 12·65%). Similarly dammaranyl B acetate gave *dammaranol B*, m. p. 117—118° depressed to 112—116° on admixture with dammaranol A, $[\alpha]_D$ +51° (*c* 0·88) (Found: C, 83·35; H, 12·7%). These compounds gave no colour with tetranitromethane or in the Halphen–Hicks test (cf. ref. 1).

Attempted Hydrogenolysis of Dammarenediol II Monoacetate.—The acetate (1 g.) in glacial acetic acid (50 ml.) was shaken with hydrogen in the presence of Adams catalyst (100 mg.). Approx. 1 mol. of gas was rapidly absorbed and no further absorption occurred after 20 hr. After chromatography and crystallisation the product was identified as dammaranediol II monoacetate by m. p. and mixed m. p. (106—108°).

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