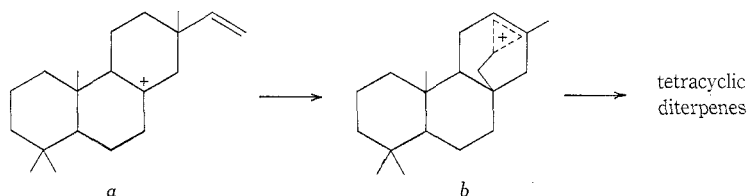


THE DEHYDRATION PRODUCTS OF SANDARACOPIMAR-15-EN-8 β -OL

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The suggestion by Wenkert¹ that the biogenesis of tetracyclic diterpenoids proceeds through the bridged carbonium ion *b* which could itself arise from a precursor *a* (Scheme 1) stimulated much activity in the cyclic diterpenoid field. The *in vitro* existence of *b* has been inferred from studies of the acid-catalysed rearrangement of tetracyclic diterpenoid skeletons² and the isolation of a tetracyclic diterpenoid from acid treatment of manool.³



Scheme 1

Removal of the hydroxyl group from the readily available sandaracopimar-15-en-8 β -ol⁴ (I) would produce the C8 carbonium ion *a*. Compound (I) was dehydrated under a variety of experimental conditions in an attempt to obtain tetracyclic products, but in all cases the only products obtained were tricyclic. These were (Table 1) isopimara-8,15-diene (II), sandaracopimaradiene (III), isopimara-7,15-diene (IV), and rimu-5(10),15-diene (V),⁵ the latter being formed as the result of a number of 1,2-migrations. Rimu-5(10),15-diene has also been isolated from the acid-catalysed rearrangement of isopimara-8,15-diene.⁶ Compound (V) was characterized by hydrogenation to rimu-5(10)-ene, which was identical with a specimen prepared by the reduction of rimu-5(10)-en-6-one⁵ with lithium aluminium hydride and hydrogenolysis of the mixture of epimeric allylic rimu-5(10)-en-6-ols. Dihydro-rimuene⁵ (20%) was also formed in this reaction.

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² Kapadi, A. H., and Dev, S., *Tetrahedron Lett.*, 1965, 1255; Sobti, R. R., and Dev, S., *Tetrahedron Lett.*, 1966, 3939; Appleton, R. A., McAlees, A. J., McCormick, A., McCrindle, R., and Murray, R. D. H., *J. chem. Soc. (C)*, 1966, 2319; Ghisalberti, E. L., and Jefferies, P. R., *Aust. J. Chem.*, 1966, 19, 1759; Buchanan, J. G. St.C., and Davis, B. R., *Chem. Commun.*, 1967, 1142; Hanson, J. R., *Tetrahedron*, 1967, 23, 793; Yoshikoshi, A., Kitadani, M., and Kitahara, Y., *Tetrahedron*, 1967, 23, 1175; Appleton, R. A., Gunn, P. A., and McCrindle, R., *Chem. Commun.*, 1968, 1131; Mori, K., and Matsui, M., *Tetrahedron*, 1968, 24, 3095; Coates, R. M., and Bertram, E. F., *Tetrahedron Lett.*, 1968, 5145.

³ Wenkert, E., and Kumazawa, Z., *Chem. Commun.*, 1968, 140.

⁴ Corbett, R. E., and Smith, R. A. J., *J. chem. Soc. (C)*, 1967, 300.

⁵ Corbett, R. E., and Wyllie, S. G., *J. chem. Soc. (C)*, 1967, 1737.

⁶ McCreadie, T., and Overton, K. H., *Chem. Commun.*, 1968, 288.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are corrected. I.r. spectra, measured on a Perkin-Elmer 421 spectrophotometer, are for liquid films or, in the case of solids, Nujol mulls. N.m.r. spectra (100 Mc/s) were measured in deuterochloroform and the chemical shifts (δ) are given as p.p.m. from tetramethylsilane. The number in parentheses following the chemical shift is the number of protons.

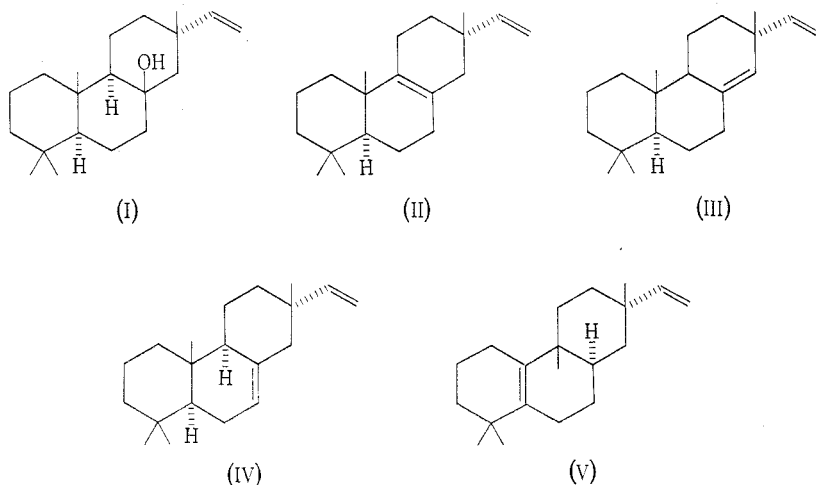


TABLE I

PERCENTAGE COMPOSITION OF MIXTURES OF HYDROCARBONS ISOLATED FROM THE DEHYDRATION OF (I) DETERMINED BY G.L.C. ANALYSIS⁷

Dehydration Method	(II)	(III)	(IV)	(V)
Thionyl chloride-pyridine	69.2	18.9	11.9	—
Formic acid-benzene	62.5	8.2	21.5	7.8
Boron trifluoride etherate	21.3	19.0	48.0	11.7
Dimethyl sulphoxide-tosyl chloride ⁸	68.6	9.5	21.9	—
Dimethyl sulphoxide ⁹	79.8	12.2	8.0	—
Mesyl chloride-collidine-dimethylformamide ¹⁰	85.0	6.0	9.0	—
Phosphorus pentachloride-hexane	41.7	40.3	18.0	—
Methyl chlorosulphite ¹¹	41.4	30.7	27.9	—

Alumina refers to Merck, standardized according to Brockmann. Preparative thin-layer chromatography (p.l.c.) was carried out on plates (20 by 20 cm) coated (1.25 mm) with silver-nitrate-impregnated silica gel, prepared from aqueous silver nitrate (15.5 g/140 ml H₂O) and silica gel H (Merck). Analytical thin-layer chromatography (t.l.c.) was carried out on plates (20 by 5 cm) coated with silver-nitrate-impregnated silica gel (0.25 mm).

⁷ Bartlet, J. C., and Smith, D. M., *Can. J. Chem.*, 1960, **38**, 2057; Carroll, K. K., *Nature*, 1961, **191**, 377; *Nature*, 1962, **192**, 965.

⁸ Nace, H. R., *J. Am. chem. Soc.*, 1959, **81**, 5428.

⁹ Traynelis, V. J., Hergenrother, W. L., Livingston, J. R., and Valicenti, J. A., *J. org. Chem.*, 1962, **27**, 2377; Traynelis, V. J., Hergenrother, W. L., Hanson, H. T., and Valicenti, J. A., *J. org. Chem.*, 1964, **29**, 123; Traynelis, V. J., and Hergenrother, W. L., *J. org. Chem.*, 1964, **29**, 221.

¹⁰ Hazen, G. G., and Rosenburg, D. W., *J. org. Chem.*, 1964, **29**, 1930.

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The analytical gas chromatograph was a Loenco 160PM fitted with dual differential flame ionization detectors. The analyses were carried out on two matched 6 ft by $\frac{1}{8}$ in. copper columns packed with Chromosorb P coated with 4% Apiezon L. The columns were operated at 200° with the detectors and injection ports at 240° and 230° respectively. The nitrogen carrier gas flowed at 60 ml/min. Under these conditions (V) was eluted first followed by (II), (III), and finally (IV).

Dehydration of Sandaracopimar-15-en-8 β -ol

Two examples of the procedures used are given. The references cited in Table 1 give experimental procedures for the other dehydrations.

(i) *Thionyl chloride*.—Compound (I) (0.30 g) in pyridine (25 ml) was treated with freshly distilled thionyl chloride (1.0 ml) at room temperature for 40 min. Dilution with water and ether extraction gave a product (0.28 g) which was filtered in hexane through alumina (30 g). Separation of the products (0.14 g) by p.l.c. using a multiple run technique gave pure (g.l.c.) isopimar-8,15-diene (75 mg), m.p. 46–48° (sublimation) (Found: C, 88.0; H, 12.1. Calc. for $C_{20}H_{32}$: C, 88.2; H, 11.8%). ν_{\max} 3080, 1633, 995, 907 (vinyl) cm^{-1} ; n.m.r., methyl signals at δ 0.87 (3), 0.90 (3), 0.99 (6); vinyl protons ABX pattern, AB(2) 4.82, X(1) 5.77 p.p.m.

The other two components present (g.l.c.) could not be separated satisfactorily.

The alkene mixture (0.10 g) was hydrogenated in ethyl acetate (15 ml) over Adams catalyst for 40 min. Filtration of the catalyst and removal of the solvent gave a mixture of three alkenes which, after separation by p.l.c. with hexane gave, in order of increasing R_F , isopimar-8(14)-ene (20 mg), isopimar-7-ene (25 mg), and isopimar-8-ene (50 mg) identical (g.l.c., t.l.c., i.r., and n.m.r.) with authentic specimens.

(ii) *Formic acid*.—Compound (I) (0.31 g) in benzene (30 ml) and 90% formic acid (5 ml) was heated under reflux for 1 hr. Dilution of the mixture with water and ether extraction gave a product which, after filtration down alumina (30 g) in hexane and separation by p.l.c. (1:99 ether-hexane) gave rimu-5(10),15-diene (V) (30 mg) and a mixture of alkenes (0.265 g) shown by g.l.c. and by hydrogenation as in (i) to be a mixture of (II), (III), and (IV). Rimu-5(10),15-diene was obtained as a colourless oil which had b.p. 60°/0.003 mm (Found: C, 87.9; H, 12.2. Calc. for $C_{20}H_{32}$: C, 88.2; H, 11.8%). ν_{\max} 3080, 1630, 998, 910 (vinyl) cm^{-1} ; n.m.r., methyl signals at δ 0.87 (3), 0.96 (9), vinyl protons ABX pattern, AB(2) 4.90, X(1) 5.80 p.p.m. Rimu-5(10),15-diene (20 mg) in ethyl acetate (10 ml) was hydrogenated over Adams catalyst for 45 min. Filtration of the catalyst and evaporation of the solvent gave rimu-5(10)-ene (18 mg), b.p. 65°/0.003 mm (Found: C, 87.6; H, 12.7. $C_{20}H_{34}$ requires C, 87.5; H, 12.5%). N.m.r., methyl signals at δ 0.82 (3), 0.83 (triplet, J 7 c/s), 0.87 (3), 0.98 (3), 0.99 (3) p.p.m.

Prolonged (3 days) acid treatment (as above) of a mixture of (II), (III), and (IV) gave (V) (10%) and (II) (90%) only.

Synthesis of Rimu-5(10)-ene

Rimu-5(10)-en-6-one⁵ (50 mg) in dry ether (15 ml) was heated under reflux with excess lithium aluminium hydride for 90 min. The ethereal solution was washed with sodium hydroxide solution (10 ml, 5*N*) and water and the solvent removed. The product was dissolved in ethanol (10 ml) containing perchloric acid (3 drops) and hydrogenated at room temperature and atmospheric pressure over 5% palladium on charcoal (15 mg) for 1 hr. Removal of the catalyst and the solvent gave a product (30 mg) which after separation by p.l.c. gave rimu-5(10)-ene (23 mg) and dihydromuene⁵ (5 mg). The synthetic specimen was identical (g.l.v., t.l.c., i.r., and n.m.r.) with the product described above.

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