128. *Miro Resin. Part II. The Resin Acids.*

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Two crystalline resin acids, both of formula $C_{20}H_{30}O_2$, have been isolated from the bled resin of *Podocarpus ferrugineus*. (1) *Miropinic acid*, m. p. 160°, $[\alpha]_D^{16°}$ — 3·6°, is tricyclic. On catalytic hydrogenation in ethyl acetate solution one of the two ethylenic linkages was reduced, resulting in the formation of two isomeric *dihydro-acids*. Each of these isomers, when further hydrogenated in acetic acid solution, yielded a different saturated *tetrahydro-acid*, together with a third *dihydro*-isomer in small amount. Miropinic acid yielded pimanthrene when dehydrogenated with selenium.

(2) iso*Miropinic acid*, m. p. 284°, $[\alpha]_D^{17°}$ + 21·2°, is present in the resin in small amount only. It is also obtained by the isomerising action of methyl-alcoholic hydrogen chloride on miropinic acid.

DURING the course of the separation of the constituents of the bled resin from the New Zealand pine *Podocarpus ferrugineus*, or Miro, 4% of resin acids were isolated (J., 1939, 1031). It is now shown that this consisted of approximately 85% of an acid, for which the name *miropinic acid* is proposed, together with 15% of an isomeric acid. Miropinic acid is only slightly soluble in 5% sodium carbonate solution but easily soluble in 4% caustic soda solution. iso*Miropinic acid* is insoluble in sodium carbonate solution and only slightly soluble in caustic soda solution.

Analyses and titrations of miropinic acid agreed with the formula $C_{20}H_{30}O_2$, but the molecular weight, determined cryoscopically in benzene solution, gave values 1·6 and 1·9 times the calculated value for this formula. However, the molecular weight of the *methyl* ester, determined cryoscopically, was in close agreement with that required for the proposed formula.

Catalytic Hydrogenation.—Miropinic acid was hydrogenated in two stages and furnished five different products. In ethyl acetate solution, with either palladium–charcoal or Adams's platinum oxide catalyst, a mixture of approximately equal amounts of α- and β-*dihydromiropinic acids* was obtained. Both products were unsaturated by the usual tests. These dihydro-isomers were further hydrogenated in acetic acid solution with platinum oxide catalyst. The α-dihydro-acid gave the saturated *α-tetrahydromiropinic acid* (yield, *ca.* 90%). The mother-liquor from the purification of this product contained a small amount of a third (γ) *dihydro-acid*. The β-dihydro-acid gave *β-tetrahydromiropinic acid* (yield, *ca.* 90%), together with a small amount γ-dihydromiropinic acid. The melting points of all the hydrogenation products were sharp and constant. The two tetrahydro-acids showed no depression in melting point when mixed, and similarly pairs of the three dihydro-acids melted gradually at intermediate temperatures. Mixtures of the dihydro- with the tetrahydro-acids all gave melting point depressions. Attempts to isomerise α-dihydromiropinic acid to the γ-form by refluxing in acetic acid solution were not successful.

Isomerisation.—Miropinic acid was not isomerised by boiling acetic acid. Preliminary isomerising experiments with boiling 95% formic acid gave a colourless resin which could not be crystallised. *iso*Miropinic acid was isolated in small amount from the unesterified residue from the preparation of methyl miropinate, indicating that miropinic acid is isomerised to some extent by alcoholic hydrogen chloride.

Dehydrogenation.—Miropinic acid gave pimanthrene in good yield when dehydrogenated with selenium.

To what extent the carbon skeleton of miropinic acid further resembles that of *d*-pimaric acid is not yet known. It is probable, judging from the resistance of the acid to esterification and of its ester to saponification, that the carboxyl group in miropinic acid is linked to a quaternary bound carbon atom. *d*-Pimaric acid, like miropinic acid, yields mixtures of dihydro- and tetrahydro-acids on catalytic hydrogenation (Ruzicka, Huyser, and Seidel, *Rec. Trav. chim.*, 1928, **47**, 363), but the physical constants of these products differ widely from those of the products obtained from miropinic acid.

Resin acids possessing melting points close to that of miropinic acid have been recorded previously. Cryptopimaric acid, isolated from *Cryptomeria japonica*, has the formula $C_{20}H_{30}O_2$ and m. p. 159—161°, but has $[\alpha]_D^{17\cdot5°}$ − 18·99° (Keimatsu, Ishiguro, and Fukuri, *J. Pharm. Soc. Japan*, 1937, **57**, 69). Cryptopimaric acid yielded pimanthrene on selenium dehydrogenation, but the degree of unsaturation was not recorded. Another acid, unnamed, of m. p. 158°, was isolated from the wood of the New Zealand tree *Dacrydium biforme* (Hosking and Brandt, *Ber.*, 1935, **68**, 1313) but was not further described. The same acid (by mixed melting point) was later obtained from the wood of *D. Kirkii* (Hosking, *N.Z. J. Sci. Tech.*, 1937, **19**, 208) and described as having a small lævorotation, formula $C_{20}H_{30}O_2$, and two ethylene linkages; it also gave pimanthrene on selenium dehydrogenation. A specimen of resin acid (m. p. 158°) extracted from a small sample of *D. biforme* wood was not depressed in melting point when mixed with miropinic acid, but the quantity was too small for the determination of optical activity. It is concluded that these acids are either identical or stereoisomeric. Miropinic acid is thus probably identical with the acid from *D. Kirkii*, although the value of the small lævorotation of this acid was not recorded.

iso*Miropinic Acid.*—When a solution of the crude, mixed resin acids in 4% aqueous caustic soda was saturated with carbon dioxide, a small amount of *iso*miropinic acid was precipitated. It had a low solubility in organic solvents and was unsaturated by the usual tests. Analyses and titration agreed with the formula $C_{20}H_{30}O_2$. It caused no depression in melting point when mixed with the acid of similar melting point and optical activity obtained by the isomerisation of miropinic acid. When *iso*miropinic acid was catalytically

reduced in acetic acid solution, a neutral unsaturated product, $C_{20}H_{30}O$, was obtained; this *substance* has not yet been further investigated.

Experimental.

Isolation of the Resin Acids.—500 G. of miro resin in ethereal solution, when shaken with 5% sodium carbonate solution, yielded only traces of acidic material. The ethereal solution was then extracted with 4% caustic soda solution; saturation of this extract with carbon dioxide precipitated 2·5 g. of crystalline *iso*miropinic acid, which was filtered off. Acidification of the filtrate with dilute sulphuric acid gave 18 g. of crystalline *miropinic acid*, which was recrystallised from methyl alcohol and washed with light petroleum, dark-coloured resinous impurities being thereby rapidly removed. Five recrystallisations gave white needles, m. p. 160° [Found: C, 79·3, 79·4; H, 10·0, 10·1; *M* (titration with 0·1N-sodium hydroxide) for a monocarboxylic acid, 301. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%; *M*, 303]. $[\alpha]_D^{16°}$ − 4·3° (10·4% solution in 1 : 1 alcohol–chloroform). After six further crystallisations from 96% alcohol the m. p. was unaltered and $[\alpha]_D^{16°}$ was − 3·6°. The acid was very soluble in chloroform or benzene, moderately easily soluble in ether or alcohol, and only slightly soluble in light petroleum. In the Liebermann reaction it gave an intense violet-red coloration. Neutral permanganate was readily absorbed in acetone solution; small amounts of bromine in chloroform solution were absorbed and in the same solvent the acid gave a faint but definite coloration with tetranitromethane.

Methyl miropinate. Miropinic acid (3·7 g.) and 4% methyl-alcoholic hydrogen chloride (22 g.) were refluxed for 2 hours, and the product poured into water. An ethereal extract was shaken with aqueous sodium hydroxide, the ether removed, and the residual *ester* (0·9 g.) distilled at 148°/0·3 mm., giving a colourless viscous oil (0·7 g.) [Found: C, 79·8; H, 10·3; *M* (cryoscopic in benzene), 315. $C_{21}H_{32}O_2$ requires C, 79·7; H, 10·2%; *M*, 316]; $d_{4°}^{20°}$ 1·032, $n_D^{20°}$ 1·5203, hence $[R_L]_D$ 93·3 (calc. for $C_{21}H_{32}O_2$ $|\overline{2}$, 93·3). Saponification of the ester at 140° in a pressure flask with 2N-alcoholic caustic potash (Found: *M*, 321) furnished the theoretical amount of acid, m. p. (after five crystallisations from methyl alcohol) 159°, not depressed by miropinic acid. Experiments at 100° and with weaker caustic potash gave lower saponification values and a proportion of ester could be recovered from the products.

Catalytic Hydrogenation.—(1) *Neutral solvent.* Miropinic acid (4 g.) in ethyl acetate was shaken in hydrogen with 10% palladium–charcoal (0·75 g.); 315 c.c. of hydrogen were absorbed during 8 minutes and no further absorption could be effected by prolonged shaking and heating ($|\overline{1}$ requires 74 c.c. of hydrogen for each g. of acid). After filtration and removal of the solvent 3·9 g. of oily crystals were obtained. On systematic crystallisation from alcohol this product was separated into approximately equal amounts of an *α-dihydro-acid*, white needles, m. p. 176°, $[\alpha]_D^{18°}$ − 10·5° (5% solution in alcohol) (Found: C, 79·0; H, 10·6%), and a *β-dihydro-acid*, white needles, m. p. 115°, $[\alpha]_D^{18°}$ + 23·2° (5% solution in alcohol) (Found: C, 78·7; H, 10·7. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%). Both dihydromiropinic acids gave a definite brown coloration with tetranitromethane in chloroform solution and absorbed bromine in the same solvent. Miropinic acid (1 g.), when hydrogenated in the same way but with Adams's platinum oxide as catalyst, furnished the same mixture of dihydro-acids.

(2) *The dihydro-acids in acetic acid.* α-Dihydromiropinic acid (0·9 g.) was dissolved in glacial acetic acid (70 c.c.) and shaken in hydrogen with 0·05 g. of Adams's catalyst. Absorption ceased after 75 minutes, 76 c.c. of hydrogen having been absorbed. The solution was filtered into water, and the crystalline precipitate recrystallised from alcohol, yielding *α-tetrahydro-miropinic acid* in white needles, m. p. 170°, $[\alpha]_D^{18°}$ + 15·2° (4·5% solution in alcohol) (Found: C, 78·3; H, 11·2. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%). The mother-liquor yielded 0·1 g. of *γ-dihydromiropinic acid*, white needles, m. p. 113°, $[\alpha]_D^{18°}$ + 46·2° (9·2% solution in alcohol, semi-micro) (Found: C, 78·7; H, 10·7. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%). β-Dihydro-miropinic acid (0·75 g.), when similarly hydrogenated, absorbed 72 c.c. of hydrogen during 85 minutes; no further reduction occurred on shaking and warming. After recovery and recrystallisations from alcohol *β-tetrahydromiropinic acid* was obtained in white needles, m. p. 170°, $[\alpha]_D^{18°}$ + 30·5° (3% solution in alcohol, semi-micro) (Found: C, 78·3; H, 11·2%). Purification of the mother-liquors gave 0·06 g. of γ-dihydromiropinic acid (by mixed m. p.), $[\alpha]_D^{18°}$ + 46·4° (7·8% solution in alcohol, semi-micro). The γ-dihydro-acid gave a faint colour with tetranitromethane in chloroform solution and absorbed bromine from the same solvent. The α- and the β-tetrahydro-acid were inert to both these reagents.

Selenium Dehydrogenation.—Miropinic acid (1·2 g.) and selenium (2 g.) were heated for 24 hours at 320—340°. Extraction of the reaction mixture with ether yielded 0·4 g. of oily crystals,

which, when distilled, gave two fractions, b. p. 150°/0·3 mm. : (1) 0·1 g., oily crystals, (2) 0·2 g., solid crystals. Fraction (2) was recrystallised from alcohol to constant m. p. 86°, not depressed by pimanthrene. Recrystallisation of fraction (1) gave a similar result. The picrate formed yellow needles, m. p. 130°, and the styphnate, yellow needles, m. p. 158°, both from alcohol; neither m. p. was depressed by the corresponding pimanthrene derivative. Oxidation of the pure hydrocarbon (0·06 g. after recovery from the picrate and styphnate by treatment with warm aqueous ammonia) with chromic–acetic acid mixture, and recrystallisation of the product, gave orange needles (m. p. and mixed m. p. 164°) of pimanthrenequinone.

iso*Miropinic Acid.*—This *acid* (2·5 g.), isolated from the crude acids, had a very low solubility in most organic solvents and was readily separated from soluble impurities by washing with alcohol, chloroform, and benzene. Recrystallisation from a large volume of acetic acid, and also from dioxan, in which it was most soluble, gave the acid in white needles, m. p. 284° [Found : C, 79·6; H, 10·1; *M* (titration with 0·1N-sodium hydroxide), 306 for a monocarboxylic acid. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%; *M*, 303]. $[\alpha]_D^{17°}$ + 21·2° (3·3% solution in dioxan).

The aqueous sodium hydroxide solution obtained during the purification of methyl miropinate was acidified and extracted with ether. Removal of the ether gave a crystalline residue (2·5 g.), which, when washed with alcohol, gave 2·3 g. of miropinic acid (identified by mixed m. p.) and left a residue (0·2 g.) which crystallised from dioxan in minute white needles, m. p. 184°, $[\alpha]_D^{17°}$ + 21·4° (0·84% solution in dioxan, semi-micro); no melting-point depression occurred on admixture with *iso*miropinic acid.

Catalytic Hydrogenation of the iso-*Acid.*—The acid (0·48 g.) was dissolved in glacial acetic acid (80 c.c.) and shaken in hydrogen with platinum oxide catalyst (0·05 g.). In the cold, 94 c.c. of gas were absorbed during 1½ hours' shaking; continued shaking and warming did not cause any further reduction. The solution was filtered into water and the resinous mass which separated on shaking was removed, dissolved in ether, and shaken with 4% aqueous sodium hydroxide; no resin acid could be extracted. The neutral material recovered from the ether could not be crystallised and on distillation at 200°/0·3 mm. gave 0·11 g. of a pale vitreous *resin* (Found : C, 83·8; H, 10·7. $C_{20}H_{30}O$ requires C, 83·8; H, 10·6%). The resin was very soluble in organic solvents, could not be crystallised, and was unsaturated to tetranitromethane and to bromine in chloroform solution.

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