407. *Synthesis of Alkylphenanthrenes. Part IV. 7-Methyl-1-ethyl- and 1-Ethyl-7-*iso*propyl-phenanthrenes: Constitution of Abietic and* d*-Pimaric Acids.*

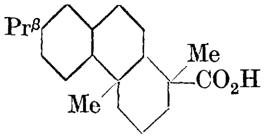
By R. D. HAWORTH.

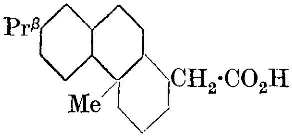
IN previous communications (this vol., pp. 1784, 2248) it has been shown that methylpimanthrene obtained from *d*-pimaric acid is not identical with 1 : 4 : 7-, 1 : 2 : 7-, 1 : 3 : 7-, or 1 : 6 : 7-trimethylphenanthrene. The remaining 1 : 5 : 7-structure appeared improbable, as it would involve a structure for *d*-pimaric acid inconsistent both with the isoprene rule and with the properties of the acid. It has been assumed previously that methylpimanthrene and methylretene are trimethyl- and dimethyl*iso*propyl-phenanthrenes, but their properties are equally concordant with the view that the two substances are methylethyl- and ethyl*iso*propyl-phenanthrene respectively.

7-Methyl-1-ethyl- and 1-ethyl-7-*iso*propyl-phenanthrene have therefore been synthesised by methods employed for the preparation of similar substances (*loc. cit.*). The former hydrocarbon, its picrate, quinone and quinoxaline correspond with methylpimanthrene from *d*-pimaric acid (Ruzicka and Ballas, *Helv. Chim. Acta*, 1924, **7**, 875) and the latter hydrocarbon, its quinone and quinoxaline correspond with methylretene (Ruzicka and Meyer, *ibid.*, 1922, **5**, 581).

These results are difficult to explain with the formulæ hitherto suggested (Ruzicka and collaborators, *ibid.*, 1931, **14**, 545; 1932, **15**, 915) and formulæ (I) and (V) or (VI) (which neglect the position of the ethylenic linkages) are now suggested for abietic and *d*-pimaric acid respectively. Formula (II), though readily accounting for the production of 1-ethyl-7-*iso*propylphenanthrene, fails in many respects; *e.g.*, it cannot be constructed from isoprene units and it does not give a satisfactory explanation of the oxidation products, $C_{12}H_{18}O_6$ and $C_{11}H_{16}O_6$, obtained from both abietic and *d*-pimaric acid (Ruzicka and collaborators, *loc. cit.*). Formula (I), on the other hand, is constructed from isoprene units and leads to structures (III) and (IV), which are in agreement with the properties of the products $C_{12}H_{18}O_6$ and $C_{11}H_{16}O_6$ respectively. Further, (I) represents abietic acid as a tertiary carboxylic acid, thus accounting for its resistance to esterification and the loss of carbon monoxide and hydrogen chloride by the action of heat on the acid chloride (Levy, *Ber.*, 1906, **39**, 3043).

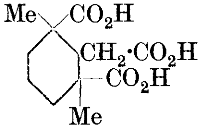
(I.)

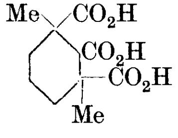




(II.)

(III.)



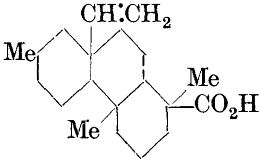


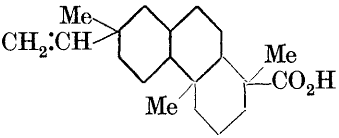
(IV.)

The production of 1-ethyl-7-*iso*propylphenanthrene from (I) involves the migration of a carbon atom from the nucleus to the side chain at some stage during the following series of operations: Ethyl abietate $\xrightarrow[\text{EtOH}]{\text{Na +}}$ abietinol $\xrightarrow{\text{PCl}_5}$ methylabietin $\xrightarrow{\text{S}}$ methylretene, and it is probable that the migration occurs during the dehydration of abietinol. The new structure for abietinol (I, with

$CH_2{\cdot}OH$ instead of CO_2H) readily accommodates a Wagner–Meerwein transformation, which occurs, either partly or completely, during the dehydration of such tertiary carbinols (cf. Ingold, J., 1923, **123**, 1706; Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3274). Further, the alternative, that the migration occurs during the dehydrogenation of methylabietin, is very improbable, as according to this view methylabietin contains a *gem*-dimethyl group, and a methyl group is eliminated when such substances are dehydrogenated (see Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 915). Abietinol loses the $CH_2{\cdot}OH$ group on sulphur treatment, in agreement with the views now advanced.

(V.)





(VI.)

Similar arguments apply to *d*-pimaric acid. A structure similar to (II) is excluded and the formulæ (V) and (VI), consistent with the isoprene rule and the properties of *d*-pimaric acid, are now suggested.

EXPERIMENTAL.

The γ-naphthyl-Δ^{β}-hexenoic acid derivatives, obtained in 85 and 90% yields by condensing MgEtI with methyl β-(6-methyl-2-naphthoyl)- and methyl β-(6-*iso*propyl-2-naphthoyl)-propionate * respectively, were solids which readily changed to resinous lactones. The crude acids were reduced with red P and HI, and the products cyclised with 85% H_2SO_4 in the usual manner. 4-Keto-7-methyl-1-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, obtained in 50% yield, was an oil, b. p. 231—233°/12 mm., yielding a *semicarbazone* which separated from EtOH in colourless nodules, m. p. 198—200° (Found : N, 14·1. $C_{18}H_{21}ON_3$ requires N, 14·2%). 4-Keto-1-ethyl-7-*iso*propyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, obtained in 60% yield, was an oil, b. p. 248—250°/19 mm., yielding a *semicarbazone* which separated from EtOH in large colourless prisms, m. p. 225—226° (Found: N, 12·9. $C_{20}H_{25}ON_3$ requires N, 13·0%). The cyclic ketones were reduced almost quantitatively by Clemmensen's method, and the products dehydrogenated by heating with Se at 300—320° for 24 hr. 7-Methyl-1-ethylphenanthrene, obtained in 60% yield, crystallised twice from EtOH, yielded colourless plates, m. p. 81° (Found : C, 92·6; H, 7·4. Calc.: C, 92·7; H, 7·3%). The picrate crystallised from MeOH in long yellow needles, m. p. 115—116° (Found : N, 9·4. Calc. : N, 9·3%), the quinone from EtOH in orange plates, m. p. 154—155° (Found : C, 81·6; H, 5·7. Calc. : C, 81·6; H, 5·6%), and the quinoxaline from AcOH in cream-

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* 6-*iso*Propyl-2-naphthoic acid, previously described as an amorphous solid (this vol., p. 1791), has now been obtained in colourless prisms, m. p. 182—183°, from aq. MeOH (Found : equiv., 216. Calc. for $C_{14}H_{14}O_2$: equiv., 214). The m. p. of the methyl ester is given incorrectly as 109—110° instead of 69—70°.

coloured needles, m. p. 154° (Found : N, 8·8. Calc. : N, 8·7%). Ruzicka and Ballas (*loc. cit.*) give 81°, 115°, 154°, and 154° as m. p.'s of methylpimanthrene, its picrate, quinone, and quinoxaline respectively. 1-Ethyl-7-*iso*propylphenanthrene, obtained in 55% yield, crystallised from EtOH in colourless plates, m. p. 79° (Found : C, 91·8; H, 8·3. Calc. : C, 91·9; H, 8·1%). The picrate separated from EtOH as a yellow ppt., m. p. 101—104°, which dissociated on heating and on attempted crystn. from EtOH. The quinone crystallised from EtOH in deep orange plates, m. p. 147° (Found : C, 81·7; H, 6·7. Calc. : C, 82·0; H, 6·5%), and the quinoxaline from AcOH in very pale yellow needles, m. p. 165—166° (Found : N, 8·2. Calc. : N, 8·0%). Ruzicka and Meyer (*loc. cit.*) give 79°, 147°, and 165° as the m. p.'s of methylretene, its quinone and quinoxaline respectively and state that the picrate is unstable.

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