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OPTICAL ROTATORY DISPERSION OF SOME PIMARENE DERIVATIVES[1]

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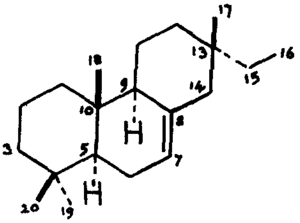
Several previous papers[2,3] have discussed the optical rotatory dispersion (O.R.D.) curves of pimarene derivatives. Corrections to the structures for isopimaric acid derivatives, chiefly due to synthetic work by Ireland et al.[3], make it necessary to review some of these results. In connection with work on araucarolone and related compounds[4], rotatory dispersion curves for several simple pimarene derivatives were determined, and we survey here the effect of the position of the endocyclic double bond and the influence of some common substituents on the plain ORD curves.

These curves were determined on a Bellingham & Stanley/Bendix-Ericsson spectropolarimeter in the spectral range 400 to 220-230 mμ, and molecular rotations $[\phi]$ at the lowest wavelength recorded are summarised in Table 1.

The Δ^7-compounds (I) all give negative plain curves with $[\phi]$ at 225 mμ generally in the range -4000 to -7000. The effects of the substituents, which are all attached in non-allylic positions, are hence insufficient to alter the sign of the curves (Table 1A). These Δ^7-compounds may be considered as stereochemically analogous to cholest-5-ene, which also gives a strong negative curve[5].

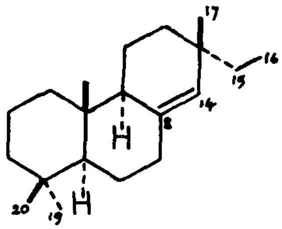
The simpler of the $\Delta^{8(14)}$-compounds (II), which have no polarisable substituent near the double bond, give plain positive curves (Table 1B); cf. cholest-4-ene, which also gives a positive curve[5]. The contributions of non-allylic substituents are small; they cannot be used to assign position or orientation of substituents.

The 8(14),15-dienes show plain curves; the sign of the curve for each compound is dependent on the configuration at the quaternary carbon atom (C-13) situated between the two double bonds (Table 1C). The isopimaradienes (III), in which the vinyl group is α-orientated, show negative curves, while the pimaradienes (IV; 13β-vinyl) show very strong positive curves. We may compare these compounds with the skewed non-conjugated diene of Mislow[6,7] (V) (cf. projections IVA and VA).



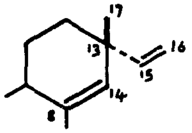
I

Isopimara-7-ene



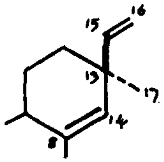
II

Isopimara-8(14)-ene



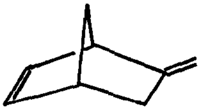
III

Isopimara-8(14),15-diene

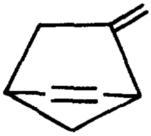


IV

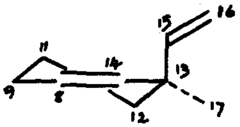
Pimara-8(14),15-diene



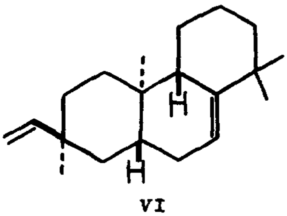
V



VA

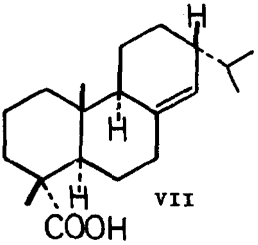


IVA



VI

Rimuene



VII

TABLE 1

Molecular Rotations (at shortest wavelength measured)
In Methanol.

	Substituents	[ϕ]	λ(in mμ)
A	Isopimar-7-enes (I)		
	16-nor	-5400	232
	16-nor-3β-hydroxy	-7600	225
	" -3α-hydroxy	-11850	224
	No substituent	-1800	232
	15-ene	-4280	230
	16-nor-15-oic acid	-5900	226
	" " ,Me ester	-3950	226
	15-ene-19-oic acid	-5150	224
	15-ene-19-hydroxy	-6120	230
B	Isopimar-8(14)-enes (II)		
	No substituent	+2730	229
	3β-hydroxy	+5320	226
	16-nor-19-oic acid	+5200	223
	19-oic acid	+1920	228

TABLE 1 (continued)

	Substituent	[ø]	λ(in mμ)
C	Isopimara-8(14),15-dienes (III)		
	3β-hydroxy	-5520	231
	19-oic acid	-5350	229
	19-oic acid,Me ester	-7900[a]	228
	Pimara-8(14),15-dienes (IV)		
	No substituent	+30600	220
	19-oic acid	+28000	217
D	16-Norpimaren-7-ols		
	8(14)-ene-7α-hydroxy	-2050	217
	8(9)-ene-7α-hydroxy	+8900	224
	8(9)-ene-7β-hydroxy	+1450	221

a In hexane

Our series closes with three allylic 16-norpimarene-7-ols (Table 1D). The epimeric $\Delta^{8(9)}$-7-ols both give positive, plain curves, which harmonize well with those reported for analogous 6β- and 6α-hydroxy-$\Delta^{5(10)}$-19-norsteroid derivatives (Ref. 7, p.55). In agreement with Mills's rule[8] for molecular rotations of allylic alcohols (at the sodium D line), the 7α-hydroxy epimer exhibits the more positive curve.

Rimuene, for which formula (VI) is now established[9], has its cyclic double bond in an environment which is essentially enantiomeric to that of a pimar-7-ene; in agreement with this it gives a positive curve. Similarly, the compound (VII) which can be included in the group of pimar-8(14)-enes is also reported to give a positive plain curve[10].

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