The Absolute Configuration of Ambonic Acid at C-25

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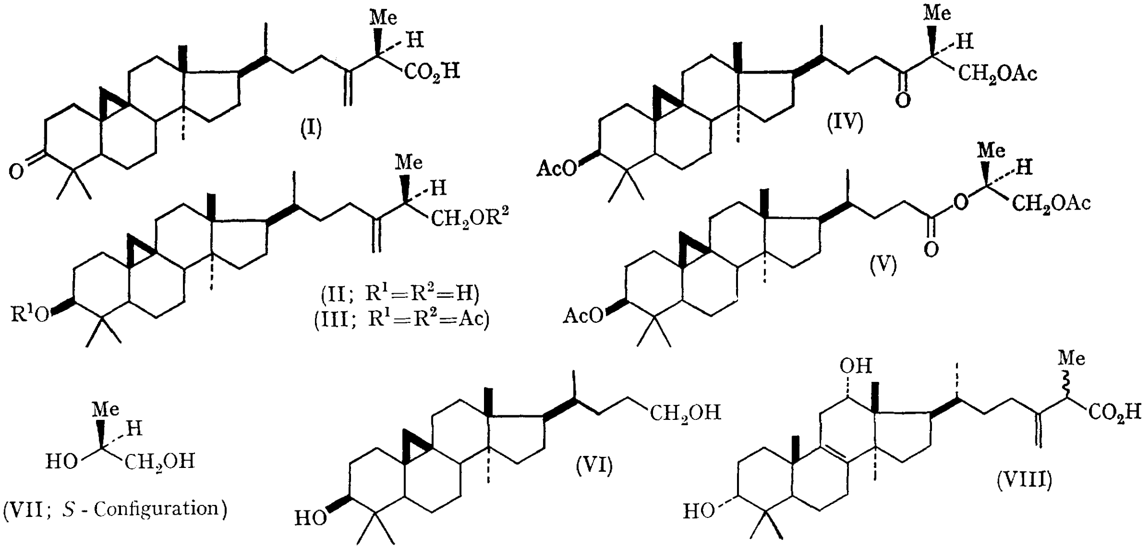
RECENTLY[1] we have elucidated the structure of ambonic acid (I), isolated from the acidic fraction of the resin of *Mangifera indica*, apart from the stereochemistry at C-25. It seems evident from the data obtained that ambonic acid possesses the *R*-configuration at C-25. $\mathrm{LiAlH_4}$ reduction of ambonic acid (I) yielded a diol (II),† m.p. 154—157°, $[\alpha]_D + 54°$, which was transformed by acylation into the diacetate (III), m.p. 83—86°, $[\alpha]_D + 55°$. Ozonolysis of compound (III) afforded the keto-diacetate (IV), m.p. 105—107°, $[\alpha]_D + 42°$. The positive Cotton effect of the o.r.d. curve of (IV) [peak at 325 mμ, $[\alpha] + 198°$ (cyclohexane)] suggested *S*-configuration at C-25 (*cf.* Djerassi's investigations of the o.r.d. of aliphatic carbonyl compounds).[2] Hence the absolute configuration at C-25 for ambonic acid would be *R* owing to the opposite sequence.[3]

This configurational assignment was confirmed as follows. Baeyer–Villiger oxidation of (IV) with trifluoroperoxy-acetic acid[4] followed by $\mathrm{LiAlH_4}$ reduction of the crude oxidation product, containing ester (V), led to the isolation, from the water-insoluble fraction, of a diol identical with an authentic sample of 24-hydroxy-25,26,27-trisnorcycloartanol (VI). From the water soluble fraction a dextrorotatory propane-1,2-diol was extracted with the same retention time on v.p.c. of an authentic sample. The propane-1,2-diol coming from the Baeyer–Villiger oxidation of (IV) showed a positive plain o.r.d. curve [$[\alpha]_{589} + 9°$, $[\alpha]_{500} + 10°$, $[\alpha]_{450} + 13°$, $[\alpha]_{400} + 85°$ (ether)] very similar with that of a sample of 2(*S*)-(+)-propane-2,3-diol (VII), obtained by $\mathrm{LiAlH_4}$ reduction of (*S*)-(−)-ethyl lactate. Since Baeyer–Villiger rearrangements occur with retention of



(I)

(II; $R^1=R^2=H$)
(III; $R^1=R^2=Ac$)

(IV)

(V)

(VI)

(VII; *S* - Configuration)

(VIII)

configuration at the migrating group,[5] the asymmetric centre at C-25 of ambonic acid must have the *R*-configuration.

These results show that the absolute configuration of β-acetoxy-ketones like (IV) can be determined from the sign of the Cotton effect. Moreover the stereochemistry at C-25 of triterpenes with the same lateral chain of ambonic acid (I), such as polyporenic acid A (VIII),[6] can be deduced from observation of the sign of the Cotton effect of the ketone corresponding to (IV).

(*Received, April* 30*th*, 1968; *Com.* 525.)

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† Diol (II) has been isolated from the neutral fraction of the resin, *cf.* S. Corsano and E. Mincione, *Ricerca Sci.*, 1967, **37**, 370.

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