425. *Studies in Relation to Biosynthesis. Part XI.* The Structure of Nalgiovensin.*

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Examination of the infrared and ultraviolet spectra of nalgiovensin, triacetylnalgiovensin, and the products of oxidation of these substances with chromic acid leads to the formula (I; R = CH_2·CHMe·OH) for nalgiovensin, in accord with prediction on the basis of its probable biosynthesis from acetic acid.

In Part V [1] was discussed the possible origin from acetic acid of many anthraquinones derived from fungi and some from higher plants. Successful use of this hypothesis in structural determinations of anthraquinones related to emodin, the triphenol corresponding to (I; R = Me), would support its validity in the anthraquinone field.

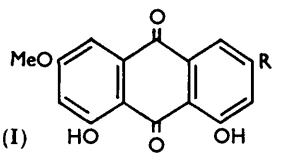
Nalgiovensin was shown by Raistrick and Ziffer [2] to be (I; R = CHEt·OH, CH_2·CHMe·OH, or CHMe·CH_2·OH). The positions of the oxygen atoms attached to the nucleus strongly suggest an acetic acid origin (II) and if the side-chain is similarly derived the most probable formula will be (I; R = CH_2·CHMe·OH).

Oxidation of the optically active nalgiovensin, $C_{18}H_{16}O_6$, by chromic acid gives an inactive substance, dehydronalgiovensin, $C_{18}H_{14}O_6$, presumably the ketone produced by

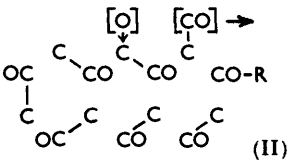
* Part X, Birch and Moye, *J.*, 1957, 412.

[1] Birch and Donovan, *Austral. J. Chem.*, 1955, **8**, 529.
[2] Raistrick and Ziffer, *Biochem. J.*, 1951, **49**, 563.

oxidation of the alcohol group. This structure is confirmed by (i) appearance of a new infrared carbonyl band at 1722 cm.$^{-1}$ (in $CHCl_3$), which can only be due to a carbonyl group in an unconjugated position, β or γ in the side-chain, and (ii) the very similar ultraviolet spectra (in EtOH) of nalgiovensin and the ketone in the region 200—400 mμ, indicating that the new carbonyl group is not adjacent to the ring. Similar oxidation of triacetylnalgiovensin, $C_{24}H_{22}O_9$, gives an optically inactive compound, $C_{24}H_{22}O_{11}$ or, more probably, $C_{24}H_{20}O_{10}$ (III) resulting from oxidation to a carbonyl group of a methylene group adjacent



(I)



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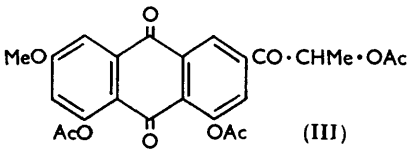

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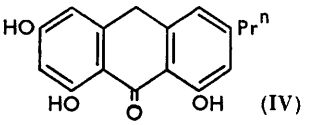

(IV)

to the aromatic ring (the racemisation is due to the position of the asymmetric centre adjacent to the new carbonyl group). The latter structure is supported by the markedly different ultraviolet spectra of triacetylnalgiovensin and its oxidation product, and a new infrared carbonyl band at 1705 cm.$^{-1}$ (in $CHCl_3$), some 17 cm.$^{-1}$ lower than that of the saturated carbonyl group in dehydronalgiovensin—the carbonyl group is therefore conjugated with the ring system. The vinyl acetate bands are at 1772 cm.$^{-1}$ in both triacetylnalgiovensin and triacetyloxonalgiovensin, but the alcoholic acetate band in the latter has shifted from 1731 to 1740 cm.$^{-1}$ by introduction of the new carbonyl group.

Nalgiovensin is reduced by hydriodic acid [2] to an anthrone which must be (IV) (or the corresponding anthranol) since, after oxidation with chromic acid and steam-distillation, paper chromatography of the volatile acids [3] showed the presence of acetic, propionic, and *n*-butyric acid.

The combined evidence proves that nalgiovensin is (I; R = CH_2·CHMe·OH) as expected, and strengthens the view that it and related substances are derived biochemically from acetic acid.

Experimental

The mould used was *Penicillium nalgiovensis* Lax., obtained from Kew and grown according to the literature.[2] The dried mycelium (60 g.) was continuously extracted with chloroform for 24 hr., the extract was evaporated to dryness, and the fats were removed by refluxing four times with light petroleum (b. p. 40—60°). The residue was dissolved in chloroform, and most of the nalgiolaxin removed by four extractions with N-sodium carbonate. The chloroform solution was evaporated to a small volume and chromatographed on magnesium silicate (Magnesol)–Celite (1 : 1) in ethyl acetate. Fairly pure nalgiovensin was obtained directly from the yellow eluate, the remaining nalgiolaxin staying on the column. Recrystallisation [2] gave nalgiovensin (400 mg.), m. p. 199·5—200·5°. The derivatives were prepared by the published routes.[2]

Infrared spectra in the region 5·5—6·5 μ (0·25% solutions in $CHCl_3$) were :

Nalgiovensin : 1615s, 1630s, 1680m, 1725w.

Dehydronalgiovensin : 1615s, 1630s, 1680m, 1722s.

Triacetylnalgiovensin : 1606s, 1675s, 1731s, 1772s.

Triacetyloxonalgiovensin : 1605s, 1675s, 1705s, 1740s, 1772s.

[3] Garbers, Schmid, and Karrer, *Helv. Chim. Acta*, 1954, **37**, 1336.

Ultraviolet spectra in EtOH were :

Nalgiovensin : max. at 225, 266, 287, 437 mμ (ε 33,800, 18,500, 16,700, 12,200); min. at 237, 276, 331 mμ (10,000, 15,700, 1290).

Dehydronalgiovensin : max. at 225, 266, 287, 437 mμ (ε 34,400, 17,900, 17,000 12,700); min. at 238, 277, 332 mμ (ε 11,500, 16,100, 2500).

Triacetylnalgiovensin : max. at 271, 346 mμ (ε 35,000, 4780); min. at 232, 311 mμ (ε 11,500, 2940).

Triacetyloxonalgiovensin : max. at 225, 243, 275, 350 mμ (ε 24,700, 25,100, 29,500, 5800); min. at 232, 258, 316 mμ (ε 23,700, 20,200, 3400).

Oxidation of Anthrone (IV).—The anthrone (IV) (25·4 mg.) was oxidised according to the method of Garbers, Schmid, and Karrer.[3] The volatile acids obtained as the mixed ethylamine salts were chromatographed on paper in butanol–water.[4] Spots were obtained corresponding to acetic (R_F 0·20), propionic (R_F 0·31), and *n*-butyric (R_F 0·49) acid; authentic acids run for comparison gave spots of identical R_F values.

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[4] Lindquist and Storgards, *Acta Chem. Scand.*, 1953, **7**, 87.