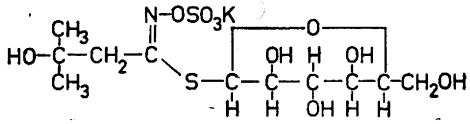

leum ether and extracted with two 1 l portions of 70 % methanol. The combined extracts were concentrated *in vacuo* to 300 ml and treated with a solution of lead acetate in order to precipitate undesired plant material. After separation of Pb-ions by H_2S the straw yellow filtrate was shortly boiled *in vacuo* until all H_2S had disappeared. The solution was filtered through a short column with 5 g of Al_2O_3 Merck and was then passed slowly through a column containing 10 ml Dowex 2-X 4 (chloride-form, 200 mesh). The effluent was free of glucoside and was discarded. After washing the resin with 200 ml of water the glucoside was eluted by 0.1 N K_2SO_4 solution. Fractions of 20 ml each were collected. The fractions 3—18 containing glucoconringiin as determined by the anthrone method and myrosinase test were brought to dryness *in vacuo*. The white residue was triturated with 3 portions of 30 ml CH_3OH at 40—50°C. The filtered methanolic solution left after evaporation *in vacuo* a colourless syrup which was dissolved in a small volume of hot 90 % ethanol. After cooling the glucoside separated partly as a viscous oil which crystallized after standing several weeks in the refrigerator. Two recrystallizations from 90 % ethanol yielded 585 mg glucoconringiin in short, white needles. F 168°C (decomp., uncorr.) $[\alpha]_D^{21}$ −10.87° (c = 3.68; in water). UV-maximum in H_2O 230.5 mμ (ε = 6 720), minimum 208 mμ (ε = 3 750). (Found: C 30.81; H 4.55; N 3.52; S 14.93. Calc. for $C_{11}H_{20}NO_{10}S_2K$ (429.51): C 30.75; H 4.69; N 3.27; S 14.93.)

The identification of the products formed by enzymatic cleavage was performed in the same way as described by Kjær *et al.*[1] for the crude glucoconringiin obtained from tetraacetylglucoconringiin. From 300 ml of glucoconringiin 82 mg of crude 5,5-dimethyl-2-oxazolidinethione were obtained which gave after two recrystallizations from benzene 32 mg of pure 5,5-dimethyl-2-oxazolidinethione, melting at 107°C alone or in mixture with a synthetic sample. Glucose was determined by paper chromatography in three solvent systems; sulfate was determined as $BaSO_4$.

For the detection of hydroxylamine as a product of hydrolysis with strong acids 10 mg of glucoconringiin were dissolved in 1 ml conc. hydrochloric acid and the solution was brought to dryness on the waterbath. The residue was taken up in 2 ml of water. After addition of about 200 mg of Na acetate the solution was further treated according to the procedure described by Blom [5].

This investigation is a part of a research project under U.S. Public Law No. 480, 83rd Congress.

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2′,5′-Dihydroxyterphenyl-2,2″-dicarboxylic Acid Dilactone

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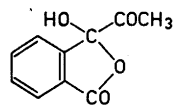
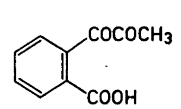
Ozonolysis of 2-methylnaphthoquinone yields methylphenylglyoxal-*o*-carboxylic acid which has a cyclic lactol structure (I) rather than the free carboxyl structure (II) [1].



I

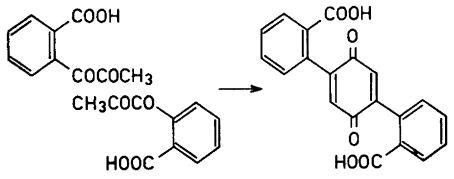


II

By briefly heating an alkaline solution of the acid a condensation product $C_{20}H_{10}O_4$ was formed in low yield. This product was sparingly soluble in most organic solvents and the melting point was very high (420—422°) without noticeable decomposition. Dissolution could be effected by ethanolic but not aqueous sodium hydroxide and

$C_{20}H_{10}O_4$ was precipitated unchanged after acidification. In concentrated sulphuric acid the substance dissolved easily with an intense light blue fluorescence.

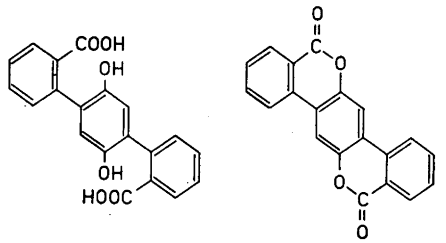
It is believed that $C_{20}H_{10}O_4$ is formed by condensation of two molecules of methylphenylglyoxal-*o*-carboxylic acid in the following way (writing the reactant in the open form for the sake of simplicity):



III

This is in close analogy to the condensation of methylphenylglyoxal in alkaline medium to 2,5-diphenylbenzoquinone [2].

In the hot alkaline medium some of the quinone III probably disproportionates giving the corresponding quinol (IV): 2′, 5′ - dihydroxyterphenyl - 2,2″ - dicarboxylic acid. On acidification this hydroxyacid is not stable, but lactonises immediately to $C_{20}H_{10}O_4$ (V).



IV *V*

The highly symmetrical structure for the condensation product is in accord with the high melting point and the low solubility of the substance. Further support comes from the spectroscopic data: A strong carbonyl band appears at 1 735 cm^{-1} which is in the lower part of the region for δ-lactones and consistent with the conjugation of the carbonyl groups with an aromatic nucleus. Aromatic absorption occurs strongly at 1 607 cm^{-1} and weakly at 1 582 cm^{-1}. The latter band must be due to the conjugated rings and is recognisable because of intensification by conjugation with carbonyl groups. Absorptions at 866 cm^{-1} and 767 cm^{-1} are probably caused by 1,2,4,5-tetrasubstitution and 1,2-disubstitution, respectively.

Our conclusion regarding the structure of $C_{20}H_{10}O_4$ is excellently borne out by X-ray crystallographic investigations [3].

Experimental. In the first experiments methylphenylglyoxal-*o*-carboxylic acid was isolated and purified before the alkali treatment. Later it was found more convenient to use directly the product from the ozonolysis in the following way:

2-Methylnaphthoquinone (5 g) in chloroform (150 ml) was ozonised at −5° until the solution became colourless. The ozonised solution was shaken with water (50 ml) and left overnight. Next day the chloroform was evaporated on a water-bath and the resulting aqueous solution filtered. To this was added aqueous sodium hydroxide (50 ml, 2 N) and the mixture boiled for a couple of minutes. In order to avoid deposition of tarry matter the alkaline solution was diluted with an equal volume of ethanol and thereafter acidified with 2 N hydrochloric acid. The dark red solution became yellow and a silky precipitate of fine needles separated (230 mg). The filtrate was made alkaline again (appr. 2 N) by the addition of solid sodium hydroxide and heated on the waterbath for 30 min. After addition of more ethanol and acidification an additional crop of needles (84 mg) was obtained. Recrystallisation was achieved with relatively large amounts of boiling glacial acetic acid. M. p. 420—422°, no decomp., crystallising again and giving the same m. p. (Found: C 76.4; H 3.3. Calc. for $C_{20}H_{10}O_4$: C 76.4; H 3.2.) The density was determined by the flotation method in mixtures of carbon tetrachloride and chloroform: $1.54 > d_{20} > 1.52$. Crystals large enough for this determination were obtained by recrystallisation from nitrobenzene.

The infrared solid-state spectra were recorded in Nujol-mull and KBr-discs with a Perkin-Elmer double beam spectrograph.

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