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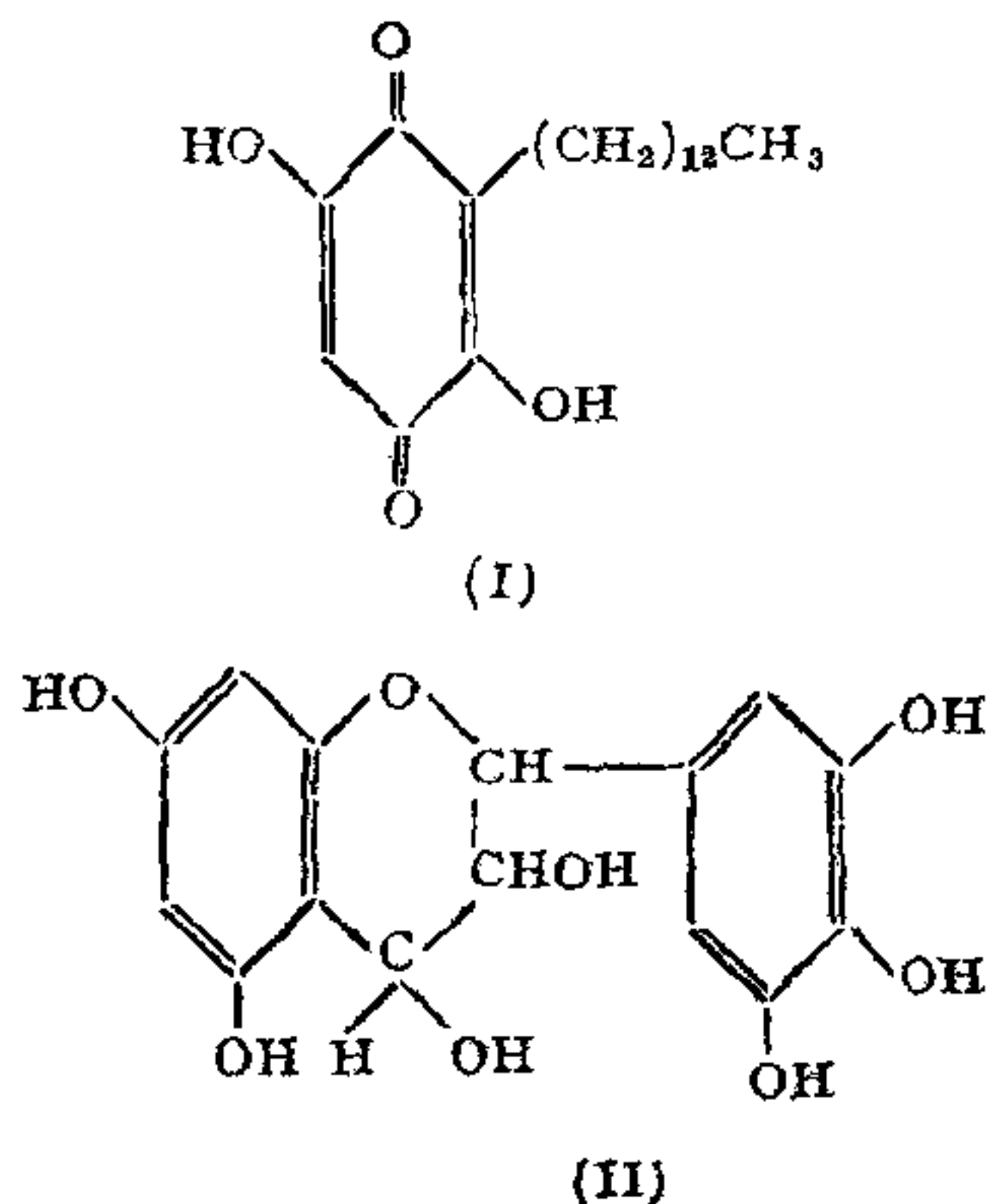
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CHEMICAL EXAMINATION OF THE BERRIES AND FLOWERS OF *ARDISIA MACROCARPA* WALL

The previous publication¹ reported the occurrence of rapanone (I) and (-) 3,4,5,7,3',4',5'-heptahydroxy-flavan (II) as the constituents from the bark and hardwood of *Ardisia macrocarpa*. We now report the chemical constituents of the berries and the flowers of *A. macrocarpa*.



Extraction of the berries with benzene gave lustrous orange plates and prisms (I), m.p. 140-41° C. (0.15%) which gave a diacetate, m.p. 64-66° C. and an acetate of its reduction product, m.p. 117-18° C. identical with rapanone and its derivatives.

The flowers of *Ardisia macrocarpa* were first extracted with pet. ether to remove waxy impurities and subsequent extraction with acetone gave a colourless product (II) as small prisms, m.p. 300° (d), from acetone, giving a heptaacetate, m.p. 228-30° C., a pentamethyl ether as colourless prisms, m.p. 184-85° C. from benzene and a diacetate of the pentamethyl ether as colourless prisms, m.p. 208-10° C. from benzene identical with (-) 3,4,5,7,3',4',5'-heptahydroxy-flavan (II) and its derivatives. It is interesting to note that products I and II present in the bark and the hardwood, are distributed in the berries and the flowers respectively.

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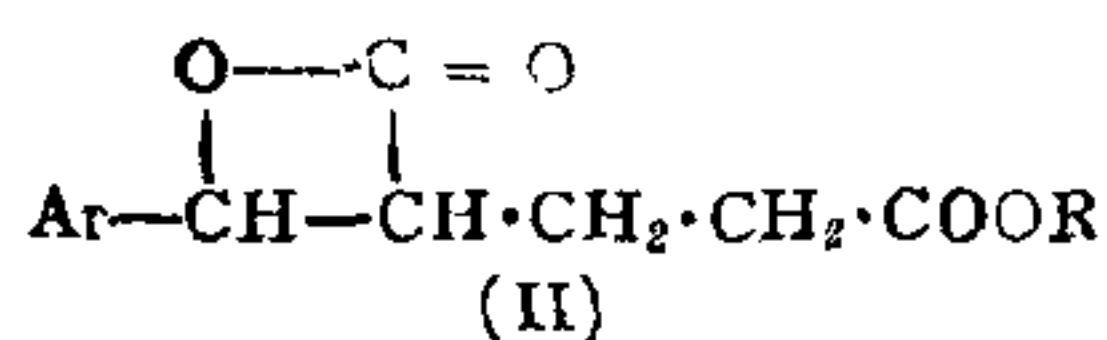
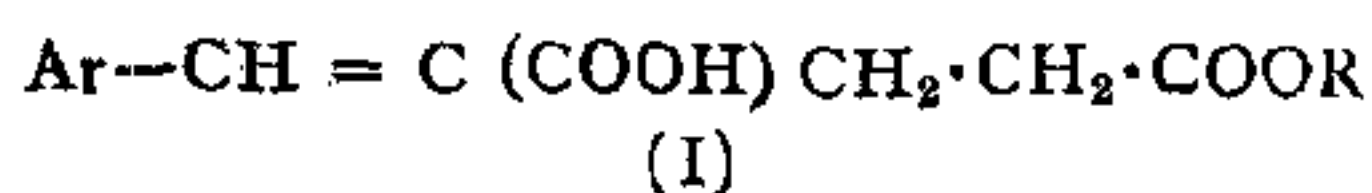
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STOBBE CONDENSATION OF ALDEHYDES AND GLUTARIC ESTERS

GLUTARIC esters have been reported earlier not to undergo the Stobbe condensation.¹ Johnson *et al.*¹ obtained a low yield (10%) of Stobbe product from ditert. butyl glutarate under specific conditions. Puterbaugh² using the stability of lithium aldols has condensed ketones with ditert. butyl glutarate. Chatterjee and Banerjee have effected a Stobbe reaction with a suitably substituted indanone and dimethyl glutarate.³

It was observed that in the presence of potassium tert. butoxide the Stobbe condensation of glutaric esters and aromatic aldehydes was a facile reaction. Good yields of oily half esters (Ia) were obtained which on hydrolysis yielded the α -arylidene glutaric acids (Ib); with 3,4-dimethoxy benzaldehyde a crystalline half ester (Ia) was isolated. I.R. Spectrum of this half ester (on comparison with the I.R. Spectra of authentic samples of 3,4-dimethoxy cinnamic acid and the corresponding ester), clearly showed an α, β -unsatu-

rated acid and a free ester group (1680 cm^{-1} and 1727 cm^{-1} respectively). This leads to the structure of the half ester as Ia (Ar = 3, 4-dimethoxy phenyl). Thus it is evident that this reaction proceeds via a β -lactone intermediate (II) and not a δ -lactone system.¹



- (a) R = Me or Et
(b) R = H

The reaction was, however, not successful when adipates or ketones were employed.

EXPERIMENTAL

A solution of dimethyl glutarate (4.0 g.) and 3, 4-dimethoxy benzaldehyde (4.15 g.) in tert. butanol (15 ml.) was added with stirring to potassium tert. butoxide (from 1 g. of potassium and 30 ml. of anhydrous tert. butanol) under an inert atmosphere. The reaction mixture was allowed to stand overnight at room temperature and then acidified with HCl (5 ml. of conc. HCl in 35 ml. of water) in cold. Most of the tert. butanol was distilled under reduced pressure and the residue was taken up in ether. The ethereal solution was extracted with sodium bi-carbonate at 0°, the alkaline phase washed with ether and acidified. The precipitated oily half ester (5.8 g.) on fractional crystallization from benzene yielded methyl γ -carboxy- γ -(3, 4-dimethoxy benzylidene) butyrate (1.2 g.), m.p. 106–7°, found: eq. wt. 294.1; C, 60.8; H, 6.14. $\text{C}_{15}\text{H}_{18}\text{O}_6$ requires eq. wt. 294.2; C, 61.2; H, 6.12%. I.R. Spectrum, 5.78 μ (ester carbonyl), 5.95 μ (α , β -unsaturated acid). Alkaline hydrolysis of the oily product yielded γ -carboxy- γ -(3, 4-dimethoxy benzylidene) butyric acid (Ib) (3.9 g.), crystals from aqueous alcohol, m.p. 192–94°, found: eq. wt. 139.2; C, 59.6; H, 5.64. $\text{C}_{14}\text{H}_{16}\text{O}_6$ requires eq. wt. 140.1; C, 59.9; H, 5.7%. I.R. Spectrum, 5.8 μ (α , β -unsaturated acid). A small quantity (0.6 g.) of 3, 4-dimethoxy benzoic acid, m.p. 180°, was also obtained from the reaction mixture.

Similarly the corresponding arylidene glutaric acids were prepared with benzaldehyde, anisaldehyde, piperonal, *o*-methoxy benzaldehyde, and *m*-chlorobenzaldehyde.

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Nagpur, December 26, 1968.

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AN EXPEDIENT FOR OVERCOMING THE INFLUENCE OF TEMPERATURE ON THE PHOTOMETRIC DETERMINATION OF SILICON IN FERROUS MATERIALS

It is well known that temperature has a distinct influence on the colour intensities that are met with in the estimation of silicon.^{1–6} Recent investigations^{7,8} from our laboratories have shown that the influence of temperature on the colour intensities involved with pure silicate solutions in different procedures could be successfully overcome by using ascorbic acid as reducing agent. However, when this reductant was employed⁹ in the colorimetric determination of silicon in cast iron, a definite increase in the colour intensities was noticed at higher temperatures. The use of a 3% ascorbic acid solution containing 0.1% stannous chloride controlled the influence of temperature to a significant extent.

Extending the investigations to the photometric determination of silicon in ferrous materials (See Ref. 2, BISRA methods), it was found that this temperature influence could be overcome by employing ascorbic acid in place of stannous chloride.¹⁰ But ascorbic acid results in lower colour intensities, about three-fourths, compared with stannous chloride. Since the latter is the most sensitive of all the reducing agents used in this field, it was considered desirable to explore the possibilities of using it, even in the tropics, by making some modifications in the procedure. It is not always very easy to provide air-conditioning facilities for maintaining lower temperatures in the works laboratories, particularly in developing countries. Also thermostating photometric cells, etc., is not easy. It, therefore, suggests itself as a possible expedient that the above difficulty may be overcome by quickly raising the temperature of the solution just before measurement to the prevailing room temperature. To examine this aspect, solutions with varying silicon contents were