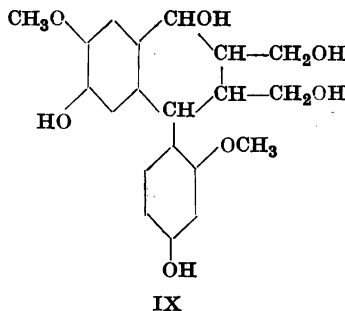
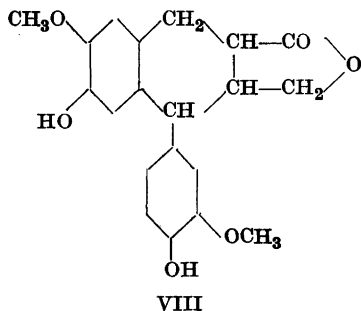
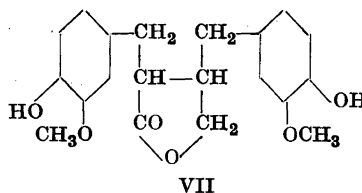
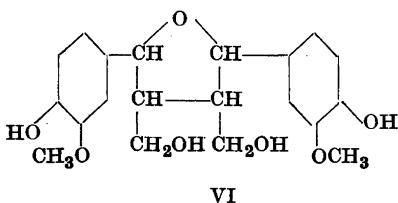
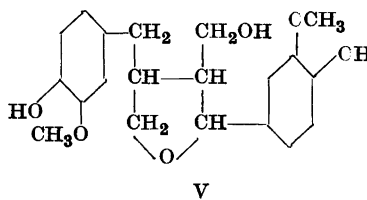
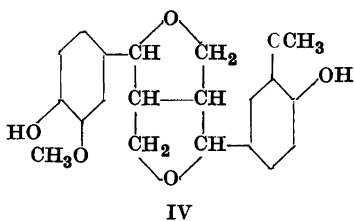


This carbon skeleton occurs in Nature in the class of compounds known as lignans⁸ — a group of substances whose relationship to lignin has been discussed by several authors^{9, 10, 11}. Recently Richtzenhain¹² obtained metahe-mipinic acid by the oxidation of acid-treated methylated lignin with potassium permanganate. The fact that only lignin which had received prior acid treatment yielded metahe-mipinic acid was considered¹³ to indicate that lignin contains structures of the type III which under the influence of acid undergo rearrangement to products of the type of VIII or IX. However, it would appear that Richtzenhain's results are capable of alternative interpretations.

The lignans pinoresinol (IV), lariciresinol (V), olivil (VI), and matairesinol (VII) may be considered to form one sub-group, conidendrin (VIII) and is-olivil (IX) falling into a special category by virtue of the fact that they contain an additional C — C linkage.



The present paper deals mainly with the oxidation of IV—IX by means of nitrobenzene and alkali — experiments similar to those carried out by Erdtman¹¹ who obtained vanillin in 24 % yield by the oxidation of pinoresinol.

Compounds IV—IX have been oxidized under the standard conditions used in our earlier experiments⁵ — conditions (reaction temp. 180°; time 2 hours; 60 ml of 2 *N* sodium hydroxide and 8 ml of nitrobenzene per g of substance) which are approximately optimal for most substances of this general type (Table 1).

In addition, a study was made of the effect of varying the alkali concentration and time of heating, on the oxidation of pinoresinol and its sulphonation product¹⁴ (Table 2).

The yields are calculated on the basis of the theoretically possible figures, and corrected for the amount of unchanged material recovered.

Pinoresinol and olivil were also heated with alkali alone at 180° for 2 hours. Pinoresinol was remarkably stable and about 60 % of the starting material

Table 1. Oxidation of IV—IX under standard conditions.

Compound	Vanillin %	Vanillic acid %	Total yield %	Unchanged material %
Pinoresinol (IV)	31	9	40	19
Lariciresinol (V)	63	5	68	0
Olivil (VI)	83	3	86	0
Matairesinol (VII)	15	2	17	0
Conidendrin (VIII)	1	—	—	—
Isoolivil (IX)	3	—	—	—

Table 2. Oxidation of pinoresinol under varying conditions.

Compound	Time hours	Alkali-conc eq/l	Vanillin %	Vanillic acid %	Total yield %	Unchanged material %
Pinoresinol	2	2	31	9	40	19
»	2	3	31	—	—	—
»	2	4	31	8	39	16
»	3	2	33	11	44	6
Barium salt of pinoresinol sulphonic acid	2	2	27	—	—	—
»	2	4	26	—	—	—
»	3	2	31	12	43	0

could be recovered; olivil, on the other hand, was completely destroyed and a dark coloured, highly insoluble condensation product was obtained in about 70 % yield.

DISCUSSION

In a previous communication ⁵ it was shown that for compounds of type I and II, provided the side chain contains several oxygen atoms or a double bond, the major factor determining the yield of vanillin is the arrangement of the carbon skeleton. For compounds of type III, however, this does not appear to be so.

Pinoresinol (IV) yields less than half the amount of vanillin obtained from olivil (VI), although both compounds contain the same carbon skeleton and differ only in the arrangement of the hydroxyl and ether groups. This is surprising in view of the fact that lariciresinol (V) yields almost as much vanillin as does olivil.

The occurrence of free primary hydroxyl groups may be of importance, as olivil contains two, lariciresinol one, and pinoresinol no such groups. Sulphonation of pinoresinol, however, does not seem to affect the vanillin yield appreciably. It seems that no simple theory will account for all the observed results and possibly the general stereochemical configuration of the molecules is of considerable importance.

The results obtained with matairesinol (VII) on the other hand are readily explained by the fact that both α -carbon atoms are unsubstituted. The small vanillin yields obtained from conidendrin (VIII) and isoolivil (IX) are completely in accordance with earlier findings ⁵, showing that a carbon atom attached to an aromatic nucleus is not split off under the conditions used.

In the same paper it was pointed out that the oxidation studies reported there might make it possible to estimate the relative amounts of "open" and "condensed" coniferyl elements in lignin. The results of the present investigation, however, indicate that, if lignin does really contain significant amounts of groupings of the type III, an estimation of this kind would be more complicated than was at first expected.

EXPERIMENTAL

The oxidation experiments and the isolation and estimation of the products formed were carried out essentially as described in the previous report ⁵. Unchanged pinoresinol was isolated as the potassium salt and identified as the diacetate.

SUMMARY

The oxidation, by means of nitrobenzene and alkali, of a number of compounds belonging to the lignan group has been studied. The results indicate

that, in this series, the arrangement of hydroxyl and ether groups has a great influence on the yield of vanillin.

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