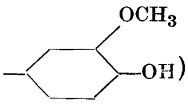
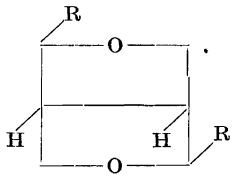
ACTA CHEMICA SCANDINAVICA 6 (1952) 1147–1151

Some New Derivatives of Pinoresinol *

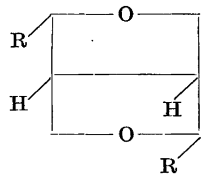
JARL GRIPENBERG and BJARNE LINDAHL

Department of Chemistry, Institute of Technology, Helsingfors, Finland

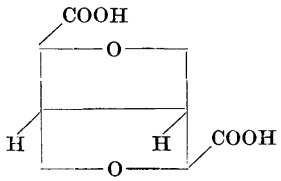
In previous papers of this series [1,2] it has been shown that pinoresinol has one of the two symmetrical configurations, I or II (R = ), but no decision concerning the correct structure has as yet been possible. If the aromatic rings could be converted into carboxylic groups (giving either III or IV) such a decision could possibly be made. Namely models of the two molecules III and IV show that in III the two carboxylic groups are in a position very close to another, so that cyclic anhydride formation should presumably be easy, whereas from IV no cyclic anhydride could be obtained.



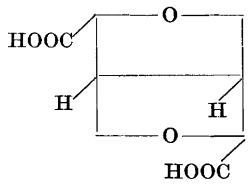
I



II



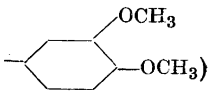
III



IV

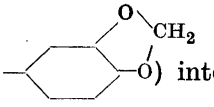
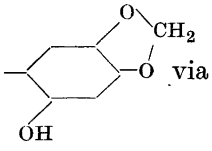
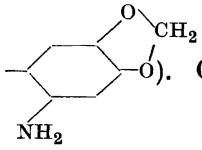
* Also XV contribution on the *Constitution of resin phenols and their biogenetic relations.* Part XIV *Acta Chem. Scand.* **4** (1950) 391.

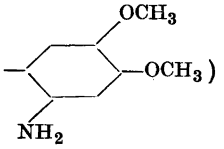
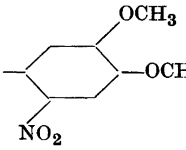
Although the preparation of the desired dicarboxylic acid could not be achieved, this investigation led to the preparation of some previously undescribed derivatives of pinoresinol, whose preparation together with a short account of the various methods tried for the oxidation of the aromatic rings in pinoresinol are described in the present paper.

Erdtman[3] oxidised pinoresinoldimethylether (I or II; R = ) with potassium permanganate and obtained veratric acid. It was however felt that if there were one free hydroxyl group, as in pinoresinol, the aromatic ring should be more susceptible to oxidation. In fact no vanillic acid was obtained on oxidation of pinoresinol in alkaline solution at room temperature, the only identifiable product being a small amount of oxalic acid.

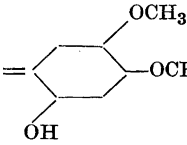
King and Grundon[4] have used hydrogen peroxide for the oxidation of the phenolic ring of tetrahydrochlorophorin to a carboxyl group. When this method was applied to pinoresinol, oxalic acid was again the only obtainable product. Oxidation with chromic acid in acetic solution gave no identifiable products.

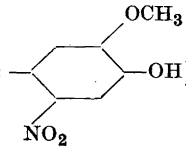
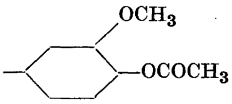
Thus as all attempts for the oxidation of the aromatic ring in either pinoresinol or its dimethylether had met with failure, the introduction of one more active group (either NH_2 or OH) in the aromatic ring was tried, in order to make this ring even more susceptible to oxidation and thus the oxidation possible under milder conditions.

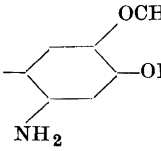
Dieterle and Schwengler[5] have described the conversion of the closely related asarinin (xanthoxylin-S) (I or II; R = ) into a dihydroxyasarinin (I or II; R = ) via diaminoasarinin (I or II; R = ). Oxidation of dihydroxyasarinin with hydrogenperoxide gave an acid, which according to Dieterle and Schwengler possibly could be the desired acid III or IV. The analytical data given by them are, however, in such a poor agreement with values calculated for $C_8H_{10}O_6$ that this claim appears highly questionable.

When this same sequence of reactions was applied to pinoresinoldimethylether, the diaminopinoresinoldimethylether (I or II; R = ) could relatively easily be obtained by catalytic hydrogenation of dinitropinoresinoldimethylether (I or II; R = ), but all attempts to obtain anything like a pure compound from the diazotisation of diaminopinoresinoldimethylether were unsuccessful.

Diaminopinoresinoldimethylether shows a remarkably high positive rotation ($[\alpha]_D^{20}$ + 255°) as compared to the rotations of dinitropinoresinoldimethylether ($[\alpha]_D^{20}$ −125°) and pinoresinoldimethylether ($[\alpha]_D^{20}$ + 64.5°).

Since the preparation of dihydroxypinoresinoldimethylether (I or II; R = ) was unsuccessful, attempts were made to oxidise diaminopinoresinoldimethylether with chromic acid to a diquinone, which on further oxidation should give the desired dicarboxylic acid, but no identifiable product could be obtained.

In order to get an even more reactive aromatic ring it was attempted to carry out the sequence of reactions mentioned above with pinoresinol. The dinitropinoresinol (I or II; R = ) has not hitherto been described. Attempted nitration of pinoresinoldiacetate (I or II; R = ) gave only unreacted starting material. Nitration of pinoresinol proved to be very dependent on the reaction conditions, but even in the best cases the yield of dinitropinoresinol was extremely poor (5—6%). In order to prove the structure of this compound its conversion into dinitropinoresinoldimethylether was attempted. However, methylation with dimethylsulphate in alkaline solution or with potassium carbonate and acetone, as well as methylation with diazomethane gave only unchanged starting material. The structure given above is thus based only on analogy with dinitropinoresinoldimethylether. The

dinitropinoresinol could be hydrogenated to diaminopinoresinol (I or II; R = ) but owing to the low yield in these reactions this approach was abandoned. Dinitropinoresinol and diaminopinoresinol do not show the very great difference in optical rotations observed with the corresponding methyl ethers.

EXPERIMENTAL

Diaminopinoresinoldimethylether. Dinitropinoresinoldimethylether (4.0 g) was dissolved in ethyl acetate, the solution warmed to about 70° and hydrogenated with a $Pt(O_2)$-catalyst at 2 atm. pressure. After 3 hours the consumption of hydrogen amounted to 540 ml (calc. 564 ml). The catalyst was filtered off from the still hot solution and the liquid concentrated. Upon cooling the diaminopinoresinoldimethylether crystallised out as colourless crystals. Yield 2.4 g (69 %). After recrystallisation from ethyl acetate it had m.p. 190—191°, $[\alpha]_D^{20}$ + 255° (c, 0.99 in chloroform). ($C_{22}H_{28}O_6N_2$ requires C, 63.4; H, 6.8; N, 6.7; found C, 63.2; H, 6.3; N, 6.4 %).

The diacetate was obtained when diaminopinoresinoldimethylether, dissolved in pyridine, was treated with acetic anhydride. It crystallised directly from the reaction mixture as microscopical needles and was purified by recrystallisation from alcohol. M.p. 289°, $[\alpha]_D^{20}$ + 117° (c, 1.02 in chloroform). ($C_{26}H_{32}O_8N_2$ requires C, 62.4; H, 6.5; N, 5.6; found C, 62.3; H, 6.4; N, 5.8 %).

The dibenzoate was obtained when diaminopinoresinoldimethylether, suspended in sodium hydroxide, was treated with benzoyl chloride. It was recrystallised from alcohol. M.p. 259°, $[\alpha]_D^{20}$ + 277° (c, 1.04 in chloroform). ($C_{36}H_{36}O_8N_2$ requires C, 69.2; H, 5.8; N, 4.5; found C, 68.7; H, 5.7; N, 5.0 %).

Dinitropinoresinol. Pinoresinol (5 g) was dissolved in propionic acid (40 ml). The solution was treated at −5° with a mixture of nitric acid (*d* 1.41, 2.6 ml) and propionic acid (10 ml). Water (400 ml) was then added and the amorphous precipitate obtained was extracted several times with chloroform. The chloroform solution was chromatographed on a column of alumina. Three different zones were obtained: a lower red, a middle light yellow and an upper brown. The lower zone gave, on further elution with chloroform and evaporation of the chloroform, dinitropinoresinol (0.34 g). Recrystallised from alcohol it formed golden yellow leaflets m.p. 184°, $[\alpha]_D^{20}$ + 20° (c, 1.01 in chloroform). ($C_{20}H_{20}O_{10}N_2$ requires C, 53.8; H, 4.5; N, 6.2; found: C, 54.0; H, 4.3; N, 6.3 %).

Diaminopinoresinol. Dinitropinoresinol (390 mg) dissolved in ethyl acetate (35 ml) was hydrogenated at 50° with a $Pt(O_2)$-catalyst at 2 atm. pressure. After 1 ½ hour 61 ml of hydrogen had been consumed (calc. 60 ml). The catalyst was filtered off and the solution evaporated to a 1/4 of its original volume. Upon cooling diaminopinoresinol (295 mg) crystallised as colourless crystals. After recrystallisation from ethyl acetate it had m.p. 216°, $[\alpha]_D^{20}$ + 59° (c, 0.196 in chloroform-metanol; 4 : 1). ($C_{20}H_{24}O_6N_2$ requires C, 62.2; H, 6.2; N, 7.2; found C, 62.0; H, 6.4; N, 6.8 %).

SUMMARY

Some new derivatives of pinoresinol have been prepared. Unsuccessful attempts have been made to oxidise the aromatic rings in pinoresinol to carboxylic groups.

REFERENCES

1. Erdtman, H. *Svensk Kem. Tid.* **48** (1936) 236.
2. Gripenberg, J. *Suomen Kemistilehti* **19 B** (1946) 138.
3. Erdtman, H. *Svensk Kem. Tid.* **50** (1938) 68.
4. King, F. E., and Grundon, M. F. *J. Chem. Soc.* **1949** 3348.
5. Dieterle, H., and Schwengler, K. *Arch. Pharm.* **277** (1939) 33.

Received October 18, 1952.