ACTA CHEMICA SCANDINAVICA 20 (1966) 2059–2066

Reactions of Lignin with Diazomethane

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The reaction between diazomethane and non-enolisable carbonyl groups in lignin is studied with appropriate model compounds and with milled wood lignin (MWL) prepared from *Picea abies*. It is shown that α- and β-carbonyl compounds (types A and B), having an aroxyl or hydroxyl group adjacent to the carbonyl group, are converted into the corresponding 1,1-disubstituted ethylene oxides. The formation of epoxide groups in MWL on treatment with diazomethane is demonstrated by the greatly diminished content of carbonyl groups in the resulting product (hydroxylamine method, IR-spectrum) and by its reaction with sodium iodide (determination of iodine). The removal of carbonyl groups during the diazomethane treatment may possibly explain two well-known properties of lignins so treated, *viz.* their high brightness and their poor ability to be sulphonated.

Diazomethane is frequently used to etherify phenolic and enolic hydroxyl groups present in lignin,[1] thus preventing them from participating in, or contributing to, certain reactions (*e.g.* Refs. 2 and 3), or spectral changes.[4,5] Furthermore, it has been shown [6] that this reagent adds to α,β-unsaturated aldehydic groups in lignin [7] to form pyrazoline structures. An additional possibility, *viz.* the reaction with non-enolisable carbonyl groups in lignin, is obvious (*cf.* Refs. 8 and 9) but has so far not been studied in detail.

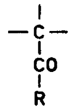
The present work was carried out in order to examine this type of reaction. Appropriate model compounds and samples of milled wood lignin (MWL), prepared from *Picea abies*, were treated with diazomethane under the conditions frequently employed in methylation experiments and the resulting products were worked up and characterised as described in the experimental section.

RESULTS AND DISCUSSION

Model experiments

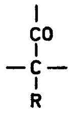
The distribution of carbonyl groups in the propane side-chains of lignin is not completely known. The results of spectrophotometric studies [5] indicate that a part (0.11/OCH_3) out of the total as determined by the hydroxylamine method[10] ($0.19/OCH_3$), is "conjugated" *i.e.* located either in the benzylic ($0.07/OCH_3$) or the allylic ($0.04/OCH_3$) position. It has been suggested that the other part ($0.08/OCH_3$), present in non-conjugated form, constitutes β-carbonyl groups.[5] In the present study, therefore, the reaction with diazomethane was investigated using model compounds of the α- and β-carbonyl types. Since treatment with diazomethane also involves methylation of the phenolic hydroxyl groups in lignin, only non-phenolic model compounds (of the 3,4-dimethoxyphenylketone types A and B) were chosen.

α-Keto compounds having an aroxyl group at the adjacent carbon atom (phenacyl-arylethers, *e.g.* I—III) reacted with diazomethane to yield products free from α-carbonyl groups (no band at 1685 cm^{-1} in the IR-spectrum,[11] no maximum at 305 mμ in the UV-spectrum[4,12]). The elemental analyses of these products were compatible with the introduction of a methylene group during the diazomethane treatment. Since no β-carbonyl band was observed in the IR-spectra (at 1710 cm^{-1}),[11] the formation of homologous (= β-) ketones (*cf.* Refs. 8 and 9) could be excluded. Thus, the methylene group was incorporated to form the corresponding 1,1-disubstituted ethylene oxides (VII—IX).



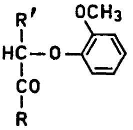
$$\begin{array}{c} | \\ -C- \\ | \\ CO \\ | \\ R \end{array}$$

A

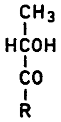


$$\begin{array}{c} | \\ CO \\ | \\ -C- \\ | \\ R \end{array}$$

B

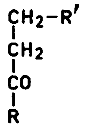


I R'=H
II R'=CH3
III R'=CH2OH



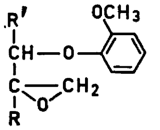
$$\begin{array}{c} CH_3 \\ | \\ HCOH \\ | \\ CO \\ | \\ R \end{array}$$

IV

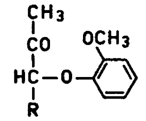


$$\begin{array}{c} CH_2-R' \\ | \\ CH_2 \\ | \\ CO \\ | \\ R \end{array}$$

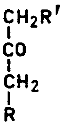
V R'=H
VI R'=OH



VII R'=H
VIII R'=CH3
IX R'=CH2OH

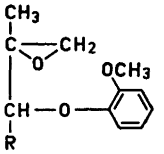


X

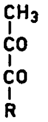


$$\begin{array}{c} CH_2R' \\ | \\ CO \\ | \\ CH_2 \\ | \\ R \end{array}$$

XI R'=OH
XII R'=H

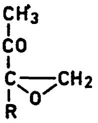


XIII

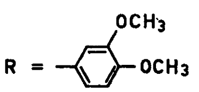


$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CO \\ | \\ R \end{array}$$

XIV



XV



A representative of these reaction products, the crystalline compound VII, was subjected to the following treatments (see Scheme 1):

1) Reaction with thiosulphate and continuous titration of the hydroxyl ions formed[13] showed the presence of 98 % of the theoretical amount of epoxy groups.

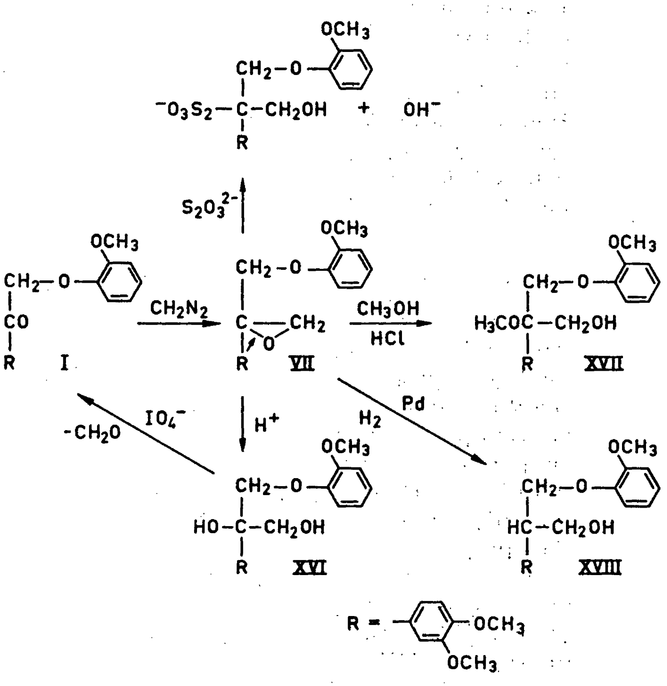
2) Treatment with phosphate buffer solution of pH 4 afforded the 1,1-disubstituted ethyleneglycol XVI. On periodate oxidation, this glycol was converted into the original carbonyl compound I (m.p. and mixed m.p.).

The liberated formaldehyde was isolated and characterised by the formation of the 2,4-dinitro-phenylhydrazone.

3) Reaction with methanolic hydrogen chloride yielded the 1,1-disubstituted ethyleneglycol monomethylether XVII.

4) Catalytic hydrogenation gave the primary alcohol XVIII. The site of ring opening and, thus, the location of the hydroxyl group was determined by treating the hydrogenation product with elemental chlorine in glacial acetic acid at room temperature.[14] No 4,5-dichloro-veratrole was formed (vapour phase chromatography), revealing that no hydroxyl group was present at the benzylic carbon atom. When exposed to the same chlorination conditions, glycol XVI gave 4,5-dichloro-veratrole in a good yield.

Scheme 1



The presence of an epoxy group in compound VII was further shown by the PMR-spectrum. The geminal protons at the epoxide ring exhibited a characteristic AB-pattern with doublets (J_{AB} = 6.0 cps) centred on 3.09 and 2.66 ppm.[15]

When the α-carbonyl compound IV, having a hydroxyl group in the β-position, was similarly treated with diazomethane, the carbonyl group disappeared, this reaction proceeding more slowly than with compound I and not going to completion. The α-carbonyl compounds V and VI, however, lacking a hydroxyl- and aroxyl group at the β-carbon atom, did not react to any considerable extent.

The *β-keto compounds* X and XI were converted by diazomethane into carbonyl-free products (IR-spectrum, *cf.* also Ref. 5, hydroxylamine method [10]). From the reaction mixture obtained after treatment of the β-keto-α-guaiacyl ether X with diazomethane, the epoxide XIII was isolated in crystalline form and characterised by analysis, IR-spectrum, m.p. and determination of the epoxy group content (thiosulphate method [13]).

3,4-Dimethoxyphenyl-acetone (XII), having neither a hydroxyl nor an aroxyl group at the α- or γ-carbon atoms, gave only a poor yield of the corresponding epoxide, even on prolonged treatment with diazomethane (*cf.* also Ref. 16).

When the diketo compound XIV was treated with diazomethane, the α-keto group was preferentially, if not exclusively, attacked. The formation of the epoxide XV was indicated by the disappearance of the α-carbonyl band and the continued presence of the β-carbonyl band in the IR-spectrum, and by the conversion of the reaction product into the corresponding 1,2-glycol on hydrolysis with an acidic phosphate buffer solution (see paragraph 2 above).

Thus, the most important structural feature for an extensive epoxide formation by the action of diazomethane appears to be an electron-attracting substituent (*e.g.* aroxyl- or hydroxyl group) at a carbon atom adjacent to the carbonyl group.[9] Such substituents decrease the electron density at the carbonyl carbon atom, thereby facilitating the nucleophilic attack by diazomethane.

Experiments with milled wood lignin

As the structural requirement mentioned above is presumably fulfilled in the majority of the carbonyl-containing phenylpropane units in lignin, diazomethane treatment of lignin preparations can be expected to result in the formation of a considerable number of epoxide groups. Experimental support for the validity of this assumption was provided by investigating diazomethane-treated MWL. This preparation showed only weak carbonyl bands in the IR-spectrum and its content of carbonyl groups, as determined by the hydroxylamine method, was only about one fourth that of the untreated MWL (*cf.* also Ref. 17). The preparation, dissolved in acetone and treated with sodium iodide in the presence of methyl red, gave a distinct yellow colour, indicating the opening of epoxide rings by iodide ions with the concomitant formation of hydroxyl ions.[18] This test gave a negative result with borohydride-reduced, diazomethane-treated MWL.

Attempts have been made to evaluate this reaction as a method of estimating the epoxide group content in diazomethane-treated MWL. The preparation was heated with sodium iodide in acetone for 4 h and the resulting product was isolated and purified by repeated reprecipitations from acetone-water. Its content of iodine was found to be 4.56 % corresponding to about 85 % of the carbonyl-groups that had reacted with diazomethane (hydroxylamine method) (see experimental section). Blanks were run with borohydride-reduced, diazomethane-treated MWL. The resulting preparations did not contain any significant amounts of iodine (less than 0.1 %).

Thus, the results of the studies carried out with model compounds and with MWL-preparations are consistent with the view that treatment of lignin with diazomethane involves not only methylation of acidic (phenolic and enolic) hydroxyl groups and addition to coniferylaldehyde structures, but also conversion of non-enolisable carbonyl groups into epoxide groups. This type of reaction may possibly explain two well-known effects of the diazomethane treatment on certain properties of lignin, such as a decrease in its ability to be sulphonated[19] and an increase in its brightness.[20] These effects find a parallel in the inhibition of sulphonation[21] and the improvement in brightness[22,23,17] brought about by treatment of lignin with borohydride. The latter reagent causes essentially an analogous structural change, *i.e.* removal of carbonyl groups. The view that these groups play an important part in the sulphonation process[21] and that they are partly responsible for the optical properties of lignin-containing materials (wood, pulp)[22] is thus further supported.

EXPERIMENTAL

All melting points are corrected. Extracts were dried over sodium sulphate and concentrated under reduced pressure. Thin-layer chromatography was performed on silica gels G and HF_{254} with chloroform or mixtures of chloroform and ethanol as solvents.[24]

The PMR-spectrum was recorded at 60 Mc/s on a Varian A 60 spectrometer. A 10 % solution in deutero-chloroform was used with a small amount of tetramethylsilane added as internal reference.

Reaction of diazomethane with model compounds

1-(3,4-Dimethoxy-phenyl)-1-(2-methoxy-phenoxymethyl)-oxirane (VII). Compound I[12] (5.0 g) was dissolved in a mixture of dioxane (50 ml) and methanol (10 ml) and to the cooled solution (ice-bath) was added a pre-cooled and dried (Na_2SO_4) ethereal solution of diazomethane prepared from nitrosomethylurea (20 g) according to Ref. 25. The mixture was kept at −4° for 6 days. The excess of diazomethane and the solvents were removed under reduced pressure at a temperature not exceeding 30°. The slightly yellowish oil obtained (5.15 g, 98.5 %) did not exhibit any band in the carbonyl region of the IR-spectrum. No maximum at 306 mμ characteristic of aromatic (= α-) carbonyl groups[12] was discernible in the UV-spectrum. The reaction product crystallised partly on standing in a refrigerator. Recrystallisation from chloroform-hexane and then from ethanol yielded lancet-shaped crystals (1.54 g), m.p. 75.5−76.5°. The mixed m.p. with the starting material (m.p. 93−94.5°) showed a distinct depression (63−65°). (Found: C 68.51; H 6.32; O 25.09; OCH_3 29.04. $C_{18}H_{20}O_5$ requires: C 68.37; H 6.33; O 25.30; OCH_3 29.42). Two characteristic four line AB-patterns were readily discernible in the PMR-spectrum, one with doublets (J = 11.0 cps) centred on 4.41 and 4.26 ppm and the other with doublets (J = 6.0 cps) centred on 3.08 and 2.67 ppm. The first one may be assigned to the protons of the acyclic methylene group, the second one to those attached to the non-substituted carbon atom of the epoxide ring.[15]

The content of epoxy groups was determined using the thiosulphate method.[13] The compound (158.1 mg, 0.5 mmole) was dissolved in acetone (5 ml) and to the solution was added a neutralised (phenolphthalein) solution of $Na_2S_2O_3.5\ H_2O$ (1.241 g) in 50 % aqueous acetone (25 ml). The hydroxyl ions liberated on refluxing the mixture were continuously titrated with 0.1 N acetic acid using an autotitrator (Radiometer Copenhague). The total consumption was 4.9 ml, corresponding to 98.0 % of the theoretical value.

The residual oil (after removal of the crystals) was analysed for epoxy groups in the same manner and found to contain 73 % of the calculated amount. Thin-layer chromatography revealed the presence of a small amount of another compound migrating more slowly (R_F = 0.6) than the main compound (epoxide VII, R_F = 0.9). Attempts to separate these two components by column chromatography on silica gel were unsuccessful because of their instability under the conditions used.

1-(3,4-Dimethoxy-phenyl)-1-[1-(2-methoxy-phenoxy)-ethyl]-oxirane (VIII) was obtained from compound II[26] by a similar diazomethane treatment and working up procedure. The resulting yellowish oil, probably containing a mixture of stereoisomeric forms of VIII, did not crystallise. The UV- and IR-spectra were similar to those of compound VII and the elemental analyses were in agreement with formula VIII. (Found: C 69.32; H 6.58; O 24.05; OCH_3 27.87. $C_{19}H_{22}O_5$ requires: C 69.11; H 6.66; O 24.23; OCH_3 28.18).

1-(3,4-Dimethoxy-phenyl)-1-[1-(2-methoxy-phenoxy)-2-hydroxy-ethyl]-oxirane (IX). On treatment with diazomethane, compound III [12] yielded epoxide IX as a viscous yellowish oil, presumably consisting of a mixture of stereoisomeric forms of compound IX (*cf.* also compound VIII, see above). No band was observed in the carbonyl region of the IR-spectrum and no maximum at 306 mμ was discernible in the UV-spectrum. (Found: C 65.55; H 6.48; O 27.26; OCH_3 26.83. $C_{19}H_{22}O_6$ requires: C 65.91; H 6.36; O 27.73; OCH_3 26.87). Acetylation of the hydroxyl group in compound IX with acetic anhydride in pyridine gave the acetate as a colourless oil. (Found: CH_3CO 12.83. $C_{21}H_{24}O_7$ requires: CH_3CO 11.08), the higher acetyl content found probably resulting from a partial opening of the epoxide ring under the acetylation conditions used.

The content of epoxy groups was determined to be 11.1 % (thiosulphate method, see above) corresponding to 91.3 % of the theoretical value.

On treatment of the product with sodium periodate in acetic acid, formaldehyde was slowly split off (isolated as 2,4-dinitrophenylhydrazone, m.p. 163—164°, not depressed on admixture of an authentic sample) and the original carbonyl compound (III) was formed (m.p. 114°, mixed m.p.).

Treatment of the α-ketol IV [27] with diazomethane gave an oil containing 70 % of the calculated value of epoxy groups (thiosulphate method). Repetition of the treatment with diazomethane did not raise the content of epoxy groups. The IR-spectrum of the reaction product showed only a weak band at 1685 cm^{-1}. Attempts to purify the epoxide by vapour phase chromatography or by preparative thin-layer chromatography were unsuccessful.

Propioveratron (V) and its β-hydroxy derivative (VI) [28] were recovered unchanged (m.p. and mixed m.p.) after the diazomethane treatment.

1-[(3,4-Dimethoxy-phenyl)-(2-methoxy-phenoxy)-methyl]-1-methyl-oxirane (XIII). When the β-carbonyl compound X [26] was treated with diazomethane in a similar manner, the yellowish oil obtained crystallised after purification by preparative thin-layer chromatography. Recrystallisation from ethanol yielded the pure compound XIII, m.p. 96—97°. (Found: C 69.07; H 6.65; O 24.33; OCH_3 28.38. $C_{19}H_{22}O_5$ requires: C 69.11; H 6.66; O 24.23; OCH_3 28.18). The content of epoxy groups was found to be 96.5 % of the theoretical value (thiosulphate method). No band was discernible in the carbonyl region of the IR-spectrum and no carbonyl groups were detected with the hydroxylamine method.[10]

Similarly, the ketol XI,[29] when treated with diazomethane, afforded a carbonyl-free product (IR-spectrum, *cf.* also Ref. 5) which gave a positive test with sodium iodide and methyl red.[18] Veratrylacetone (XII) [30] however, reacted only to a limited extent, the resulting oil containing about 80 % of the carbonyl groups of the starting material (hydroxylamine and borohydride method) and exhibiting a distinct β-carbonyl band at 1715 cm^{-1}.

When veratroyl-acetyl (XIV) [31] was treated with diazomethane, the α-carbonyl band (at 1685 cm^{-1}) disappeared, whereas the β-carbonyl band (at 1715 cm^{-1}) in the IR-spectrum remained unchanged. The resulting oil was heated in a phosphate buffer solution of pH 6 to yield a 1,2-glycol. The 1,2-glycol structure was confirmed by the periodate-benzidine test.[32] The continued presence of a carbonyl group in this glycol was shown by conversion into the 2,4-dinitrophenylhydrazone derivative which, after recrystallisation from ethanol, melted at 260-262°. (Found: C 52.20; H 4.42; O 27.18; N 15.82; OCH_3 17.75. $C_{18}H_{20}O_8N_4$ requires: C 51.41; H 4.80; O 30.46; N 13.33; OCH_3 14.78). Attempts to further purify this 2,4-dinitro-phenylhydrazone by various chromatographic methods were unsuccessful.

Reactions of the epoxide VII

1-(3,4-Dimethoxy-phenyl)-1-(2-methoxy-phenoxymethyl)-1,2-dihydroxy-ethane (XVI). The epoxide VII (1 g) was dissolved in dioxane (30 ml) and a phosphate buffer solution of pH 4.9 (90 ml) was added. The mixture was heated at 135° for 24 h and then extracted with chloroform. Purification of the resulting oil by preparative thin-layer chromatography gave the crystalline 1,2-glycol XVI (0.76 g, 72 %) a sample of which was recrystallised twice from ethanol, m.p. 129—130°. (Found: C 64.55; H 6.80; O 28.81; OCH_3 27.30. $C_{18}H_{22}O_6$ requires: C 64.69; H 6.58; O 28.73; OCH_3 27.84).

On treatment of compound XVI (1 mmole) with elemental chlorine in glacial acetic acid,[14] 4 mmoles of chlorine were rapidly consumed and 4,5-dichloro-veratrole was formed (vapour phase chromatography).

When oxidised with periodate according to Ref. 33, compound XVI (1 mmole) consumed 0.98 mmole of the oxidant. The resulting precipitate was filtered off, purified by preparative thin-layer chromatography and by recrystallisation from ethanol. It proved to be identical with the parent carbonyl compound I (m.p. 91—92°, mixed m.p. 90—92°). The aqueous filtrate was evaporated *in vacuo*. The formaldehyde released during the periodate-oxidation was isolated from the distillate as the 2,4-dinitro-phenylhydrazone derivative, m.p. 162—164°.

1-(3,4-Dimethoxy-phenyl)-1-(2-methoxy-phenoxymethyl)-1-methoxy-2-hydroxy-ethane (XVII). The epoxide VII (0.5 g) was dissolved in methanol (10 ml) and 1.1 % methanolic hydrogen chloride (1 ml) was added. The reaction was complete after a few minutes (thin-layer chromatography). Neutralisation of the solution with 0.2 % methanolic sodium hydroxide, evaporation to dryness and extraction of the residue with chloroform gave crystals which were recrystallised from isopropanol to yield needles (325 mg, 57.5 %) melting at 80—80.5°. (Found: C 65.30; H 6.91; O 27.72; OCH_3 35.10. $C_{19}H_{24}O_6$ requires: C 65.54; H 6.89; O 27.57; OCH_3 35.62).

1-(3,4-Dimethoxy-phenyl)-1-(2-methoxy-phenoxymethyl)-2-hydroxy-ethane (XVIII). The epoxide VII (200 mg) was dissolved in ethanol (50 ml) and catalytically hydrogenated (Pd on charcoal). The theoretical amount of hydrogen (14.2 ml) was consumed after 10 min. The reaction product was purified by preparative thin-layer chromatography. It started to crystallise after having been kept in a refrigerator for about 2 weeks. No appropriate solvent could be found for recrystallisation. (Found: C 67.94; H 7.05; O 24.96; OCH_3 29.81. $C_{18}H_{22}O_5$ requires: C 67.94; H 6.91; O 25.14; OCH_3 29.24).

On chlorination of compound XVIII with elemental chlorine in glacial acetic acid, no 4,5-dichloro-veratrole was formed (vapour phase chromatography).

Experiments with milled wood lignin (MWL)

MWL was prepared from *Picea abies* essentially according to Ref. 34. Its methoxyl content was 15.3 %, its carbonyl content 1.62 % (hydroxylamine method). Thus, a considerably lower CO/OCH_3 ratio (0.117) was found than that reported previously for MWL's (0.19).[10] The discrepancy in the carbonyl contents of different MWL-preparations may possibly be explained by different conditions employed during the grinding, extraction, and purification procedures (lengths of time, temperature, solvents *etc.*). The lower value found for the preparation used in the present work agrees with that reported for Brauns' lignin.[10]

Treatment of MWL with diazomethane. A sample (10 g) of this MWL preparation was dissolved in dioxane (100 ml) and methanol (20 ml). The solution was cooled (ice) and an excess of diazomethane, prepared from 80 g nitrosomethylurea [25] and dissolved in dioxane, was added. After standing in a refrigerator for one week the excess of diazomethane and the solvents were removed by evaporation under reduced pressure at a temperature not exceeding 30°. The yellowish residue (about 12 g) was dissolved in dichloroethane-ethanol (2:1) (300 ml) and the solution was added dropwise to vigorously stirred ether (3 l). The almost white precipitate was centrifuged off and washed twice with ether and once with petrol ether. After drying *in vacuo* over P_2O_5 and paraffin wax a slightly pale powder (10.5 g) was obtained (OCH_3 19.47 %). The IR-spectrum of this lignin preparation showed a greatly diminished α-carbonyl band (at 1665 cm^{-1}), whereas the weak β-carbonyl band (at 1715 cm^{-1}) appeared to be only slightly reduced. Estimation of the carbonyl groups by the hydroxylamine method revealed that about 3/4 ($0.086/OCH_3$) of the amount originally present ($0.117/OCH_3$, see above) had been removed during the diazomethane treatment.

Attempts to determine epoxy groups in diazomethane-treated MWL. Diazomethane-treated MWL (0.5 g) was dissolved in 90 % aqueous acetone (5 ml) and a solution of sodium iodide (1.5 g) in acetone (10 ml) was added. The mixture was refluxed for 4 h. then cooled and dropped into vigorously stirred water (100 ml). The resulting precipitate was centrifuged off and carefully washed with water until the washings were free from iodide ions. This crude product was redissolved in aqueous acetone and reprecipitated by dropping the solution into water to ascertain that no iodide ions were adsorbed on the reaction product. After washing with water and drying *in vacuo* over P_2O_5 the preparation was analysed for iodine and found to contain 4.56 %. From this value, a ratio I/OCH_3 = epoxy groups/OCH_3 of 0.0735 can be calculated corresponding to about (85 %) of the carbonyl groups which had reacted with diazomethane (0.086/OCH_3, see above).

Borohydride-reduced, diazomethane-treated MWL, when similarly heated in a solution of sodium iodide in acetone and purified by reprecipitation, gave a product which was found to contain less than 0.1 % iodine.

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Received April 21, 1966.