Notes

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Organic Analysis. XXXVII.[*1] Reaction Mechanism of Mannuronic Acid and Galacturonic Acid with 1,3-Naphthalenediol.

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In the previous papers[1,2] of this series, the reaction mechanism of glucuronic acid with 1,3-naphthalenediol was clarified in the Tollens reaction[3] and also in the fused reaction.[4] This paper extends the study to the other hexuronic acid, mannuronic acid and galacturonic acid.

In the Tollens reaction of glucuronic acid, two dyes were obtained as their methyl ethers, Dye I-methyl ether (I) and Dye Ⅱ-methyl ether (Ⅱ). Now, the ethers could be separated on a paper chromatogram when developed with benzene-petroleum benzin-water (1:5:1), showing the Rf values of 0.19 for (I) and 0.51 for (Ⅱ). In the same reaction of mannuronic acid and galacturonic acid, the coloring matters formed were methylated, and a preliminary study was carried out on the paper chromatogram using the above solvent. Two red violet spots of Rf values of 0.19 and 0.51 were obtained in both cases. Therefore, the separation of the coloring matters was carried out in the same way as in the previous paper, and methyl ethers of Dye I and Dye Ⅱ obtained were identified, respectively, by the melting points of admixture and also by the infrared spectra.

Mannuronic acid and galacturonic acid showed the same coloration as glucuronic acid when they were fused with 1,3-naphthalenediol at 120∼130°. The methylated coloring matters gave four red violet spots of Rf values of 0.19, 0.51, 0.71, and 0.85 on the paper chromatogram. The first two dyes corresponded to the above methyl ethers, and the last two spots were identified as the spots of Dye Ⅲ-methyl ether and Dye Ⅳ-methyl ether, respectively, which were obtained in the fused reaction of glucuronic acid. These four dyes were also separated by the chromatography on alumina with benzene as eluant by the method described previously.[2]

These results proved that mannuronic acid and galacturonic acid reacted with 1,3-naphthalenediol in the same mechanism as glucuronic acid both in the Tollens reaction and in the fused reaction.

Experimental

Paper Chromatography——This was carried out by the ascending method with Toyo Roshi No. 51. The developing solvent was mixed in the volume mentioned before, and the resultant upper layer was used.

Isolation of the Dyes——Both Tollens reaction and fused reaction of mannuronic acid or galacturonic acid and the following isolation of the dyes were carried out in the same way as in the previous papers.[1,2] The yielded Dye I-methyl ether, m.p. 241∼242°, Dye Ⅱ-methyl ether, m.p. 294∼295°, Dye Ⅲ-methyl ether, m.p. 268∼270°, and Dye Ⅳ-methyl ether, m.p. 258°, were identified, respectively, by the melting points of admixture and by the infrared spectra as the corresponding methyl ethers which were obtained from glucuronic acid.

[*1] Part XXXVI : This Bulletin, **10**, 553 (1962).

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1) T. Momose, Y. Ueda, M. Iwasaki : This Bulletin, **4**, 49 (1956).

2) *Idem* : *Ibid.*, **10**, 546 (1962).

3) B. Tollens, F. Rorive : Ber., **41**, 1783 (1908).

4) A.H. Guerrero, R.T. Williams : Nature, **161**, 930 (1948).

Summary

In the Tollens reaction and fused reaction, mannuronic acid and galacturonic acid proved to react with 1,3-naphthalendiol in the same mechanism as glucuronic acid by isolating the coloring matters in a crystalline form.

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Synthesis of Nor-Juzunol.[1]

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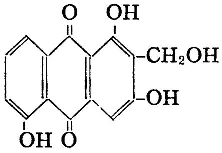
In the previous paper[1] the synthesis of nor-juzunol whose structure corresponded to 2-hyroxymethyl-1,3,5-trihydroxyanthraquinone (I) was reported. This paper is concerned with confirmation of the position of a hydroxymethyl group in the molecule of 1,3,5-trihydroxyanthraquinone (II).



(I)

Direct condensation of *m*-hydroxybenzoic acid (III) and 4-methyl-α-resorcylic acid (IV) by conc. sulfuric acid and boric acid gave 2-methyl-1,3,5-trihydroxyanthraquinone (V), m.p. 280°, whose infrared spectrum showed bands at 3367 cm^{-1} (OH), 1608 cm^{-1} (chelated C=O) and 1563 cm^{-1} (phenyl), and no absorption of non-chelated C=O as shown in Fig. 1. In this condensation 1,5-dihydroxy-, and 2,6-dimethyl-1,3,5,7-tetrahydroxyanthraquinone were also obtained. 2-Bromomethyl-1,3,5-trihydroxyanthraquinone triacetate (VII), m.p. 242~244°, obtained by bromination of the triacetate (VI), m.p. 239.5~240.5°, of (V) with N-bromosuccinimide, was then converted into 2-hydroxymethyl-1,

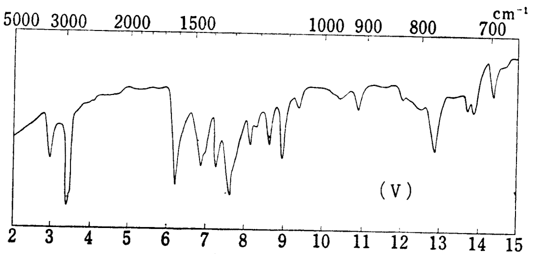
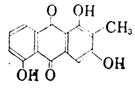


Fig. 1



(V)

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[1] Y. Hirose : This Bulletin, 8, 417 (1960).