hydrazine and glacial acetic acid in aqueous solution as had been reported by Brigl and Schinle.[8] The analysis for the glucose phenylosazone is as follows.

Anal. Calcd. for $C_{18}H_{22}O_4N_4$: N, 15.64; OCH_3, 0.00. Found: N, 15.93; OCH_3, 0.40.

The *p*-toluidide of 2-methylglucose was prepared by heating 1.04 g. of the monomethyl sugar (OCH_3, 15.27%) with 0.72 g. of *p*-toluidine and 0.30 ml. of water. The mixture was heated on a water-bath until the solution became homogeneous and for ten minutes thereafter to insure complete reaction. After cooling, 2 ml. of 95% ethanol and 4 ml. of ether was added. Cooling in the refrigerator yielded a precipitate (0.15 g.) that was identified as unchanged 2-methylglucose. The mother liquor was evaporated to 1.5 ml. and left overnight; needle-like crystals (0.55 g.), m. p. 150–151° after purification, were obtained.

Anal. Calcd. for $C_{14}H_{21}O_5N$: OCH_3, 10.95. Found: OCH_3, 10.7.

Prolonged refluxing in the water–ethanol solvent with dilute acetic acid and with dilute hydrochloric acid gave no evidence for the Amadori rearrangement; crystals of the glucoside were isolated in all cases.

Summary

Physical properties are reported for a number of glucosylalkylamines and the corresponding glucamines.

The glucamines formed from primary amines of intermediate molecular weight are good wetting agents.

An approximation of the degree of hydrolysis of the various N-substituted glucosides was made by comparison of changes in rotation, by potentiometric titration and by extraction of the hydrolyzed amine. With the exception of the first member of the series, 1-aminoglucose, ease of hydrolysis appears to parallel the K_B of the nitrogen substituent.

An attempt was made to effect the Amadori rearrangement of the glucosylalkylamines and the acyl derivatives of 1-aminoglucose. No rearranged product could be isolated in either case.

The *p*-toluidide and phenylhydrazine derivative of 2-methylglucose were prepared. The methoxyl group on the second carbon atom prevented rearrangement of the *p*-toluidide, but glucose phenylosazone was prepared from the phenylhydrazine derivative of 2-methylglucose.

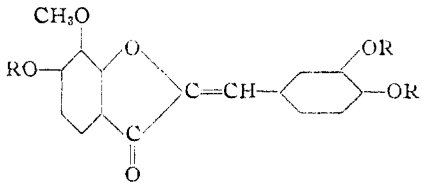
AMES, IOWA RECEIVED AUGUST 23, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

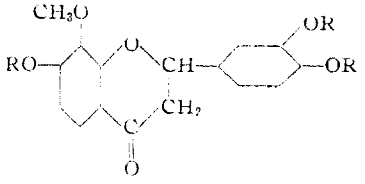
Anthochlor Pigments. V. The Pigments of *Coreopsis grandiflora*, Nutt. II

BY T. A. GEISSMAN AND CHARLES D. HEATON

In the preceding paper of this series,[1] structures were proposed for leptosin, leptosidin and a flavanone, constituents of the flower petals of *Coreopsis grandiflora*, Nutt. Leptosin and leptosidin are related as glycoside and aglycon, and to the latter was assigned the structure of 7-methoxy-3′,4′,6-trihydroxybenzalcoumaranone (I). The position of the sugar residue (presumably glucose) in leptosin was assumed to be 6, on the basis of certain distinctive color reactions of the glycoside. The structure of the flavanone was considered to be II, both because of the correspondence in the positions of the hydroxyl and methoxyl groups in this structure and in that chosen for leptosidin, and because of the similarity between certain color reactions of the flavanone and those of butin (3′,4′,7-trihydroxyflavanone).



I, R = H
III, R = CH_3



II, R = H
IV, R = CH_3

We have synthesized 3′,4′,6,7-tetramethoxybenzalcoumaranone (III) by the condensation of veratraldehyde with 6,7-dimethoxycoumaranone. The product, crystallizing in bright yellow needles, did not depress the melting point of fully methylated leptosidin. This establishes for the first time the occurrence in nature of a substance possessing the benzalcoumaranone nucleus.

3′,4′,7,8-Tetramethoxyflavanone (IV) has been described by Kostanecki and Rudse,[2] who reported its melting point as 144°. While the trimethyl ether of the naturally-occurring flavanone analyzed correctly for this structure and showed color reactions which left no doubt that it was a flavanone and pointed strongly to the probability that it had structure IV, it melted at 139–140°, a fact which left some doubt as to its identity with the flavanone described by Kostanecki and Rudse. The synthesis of IV has shown that the trimethyl ether of the naturally-occurring flavanone is indeed 3′,4′,7,8-tetramethoxyflavanone. The condensation of gallacetophenone 3,4-dimethyl ether with veratraldehyde yielded 2′-

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(1) Geissman and Heaton, THIS JOURNAL, **65**, 677 (1943).

(2) Kostanecki and Rudse, *Ber.*, **38**, 937 (1905).

hydroxy-3′,4′,3,4-tetramethoxychalcone, and this was isomerized to the flavanone by treatment with dilute alcoholic hydrochloric acid. The product melted at 137–139° even after repeated recrystallization from dilute alcohol, and retained a pale yellow color. It did not depress the melting point of the natural substance and gave the same blue-violet color when reduced with magnesium and alcoholic hydrochloric acid. Further study showed that it was contaminated with a small amount of the chalcone, and when this was removed the pure flavanone, m. p. 143.5–144°, was obtained. A mixture of this material and that obtained from the natural source melted at 142.5–143°.

The position of the methoxyl group in leptosidin and in the flavanone, and the point of attachment of the sugar residue in leptosin still rest upon the inferences drawn from the observations previously reported.[1] These inferences carry additional weight in view of the establishment of the disposition of the oxygen atoms in these compounds, but direct proof is still needed and will be the object of further work.

Experimental

6,7-Dimethoxycoumaranone.—To a suspension of 4.0 g. of α-chlorogallacetophenone[3] in 30 ml. of hot water was added 12 g. of sodium carbonate, followed by 10 ml. of dimethyl sulfate, with stirring. After the reaction was complete, an additional 6 g. of sodium carbonate and 3 ml. of dimethyl sulfate were added and the mixture warmed for a few minutes longer. The semi-solid mixture was filtered and the solid removed and stirred with warm alcohol to remove inorganic salts. Upon cooling the alcoholic solution the product separated as reddish crystals. Recrystallized from alcohol, the compound formed light pink crystals, m. p. 122–123°[4] (literature,[5] m. p. 122°).

3′,4′,6,7-Tetramethoxybenzalcoumaranone (III).—A solution of 0.5 g. of veratraldehyde and 0.5 g. of 6,7-dimethoxycoumaranone in 10 ml. of warm alcohol was treated with 3 ml. of 30% aqueous sodium hydroxide solution. Yellow crystals began to form at once and in less than a minute the reaction mixture had set to a crystalline mass. The product (0.68 g., 84%) was collected and recrystallized from aqueous alcohol. The bright yellow needles melted at 156–157° and further recrystallization did not change the melting point. A mixture of the synthetic material with leptosidin trimethyl ether (m. p. 156–157°) melted at 156–157°.

2′-Hydroxy-3′,4′,3,4-tetramethoxychalcone.—A solution of 0.5 g. of gallacetophenone 3,4-dimethyl ether[6] and 0.45 g. of veratraldehyde in 4 ml. of warm alcohol was treated with 2 g. of hot 50% sodium hydroxide solution. The mixture was shaken and kept hot for fifteen minutes, cooled and poured into dilute hydrochloric acid. The oily precipitate solidified on standing. It was recrystallized from dilute alcohol, yielding 0.51 g. of yellow-orange needles, m. p. 121–122° (literature,[2] 119°).

3′,4′,7,8-Tetramethoxyflavanone (IV).—A solution of 0.25 g. of the chalcone in a mixture of 20 ml. of alcohol, 8 ml. of concentrated hydrochloric acid and 25 ml. of water was refluxed for four hours, evaporated to half its volume and poured into dilute hydrochloric acid. The yellow oil which separated soon solidified. After seven recrystallizations from dilute alcohol the flavanone was still pale yellow in color and melted at 137–139° (literature,[2] 144°). A mixed melting point with the fully methylated naturally-occurring flavanone, m. p. 139–140°, was 138–140°. The two substances gave identical colors when reduced side by side with magnesium and alcoholic hydrochloric acid.

The synthetic material was recrystallized from carbon disulfide, and careful examination of the product showed that it was a mixture of yellow-orange rosets and pale yellow needles. A partial mechanical separation of these two substances, followed by recrystallization of the nearly colorless material from carbon disulfide, afforded nearly colorless needles of the pure flavanone, m. p. 143.5–144°. A mixture of this material with the natural substance (m. p. 139–140°) melted at 142.5–143°.

Anal. Calcd. for $C_{19}H_{20}O_6$: C, 66.26; H, 5.86. Found: C, 66.10; H, 5.92.

Summary

Leptosidin trimethyl ether and the trimethyl ether of the flavanone accompanying leptosidin in the flower petals of *Coreopsis grandiflora*, Nutt, have been identified as 3′,4′,6,7-tetramethoxybenzalcoumaranone and 3′,4′,7,8-tetramethoxyflavanone, respectively.

The proof of the structure of leptosidin trimethyl ether establishes for the first time the occurrence in nature of a compound possessing the benzalcoumaranone nucleus.

LOS ANGELES, CALIFORNIA RECEIVED AUGUST 19, 1943

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[3] Nencki, *J. Russ. Phys.-Chem. Soc.*, **25**, 182 (1883).

[4] Melting points are uncorrected.

[5] Felix and Friedländer, *Monatsh.*, **31**, 63 (1910).

[6] Baker, Jukes and Subrahmanyam, *J. Chem. Soc.*, 1682 (1934).