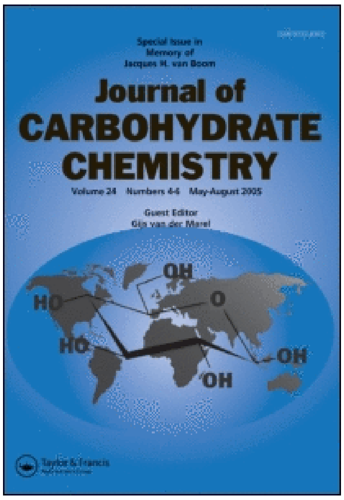

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James C. Goodwin[a]
[a] U.S. Department of Agriculture, Northern Regional Research Center, Agricultural Research Service, Peoria, Illinois

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SODIUM COMPLEXES OF ISOMALTOL AND MALTOL *

James C. Goodwin
Northern Regional Research Center,
Agricultural Research Service,
U.S. Department of Agriculture,
Peoria, Illinois 61604

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ABSTRACT

Sodium bis(3-O-hydroxy-2-furyl methyl ketone) (3) and sodium 3-O-hydroxy-2-methyl-4-pyrone hydrate (4) were isolated and characterized from the interaction of isomaltol and maltol with sodium methoxide in boiling benzene (toluene or acetone). Elemental analyses of 3 furnished the formula $C_{12}H_{11}NaO_6$, and this composition was confirmed by conversion to isomaltol O-benzoyl ester.

INTRODUCTION

Several covalent complexes of alkali metals with enolic forms of β-keto-esters, β-diketones, aldehydes and oximes have been described.[1-12]

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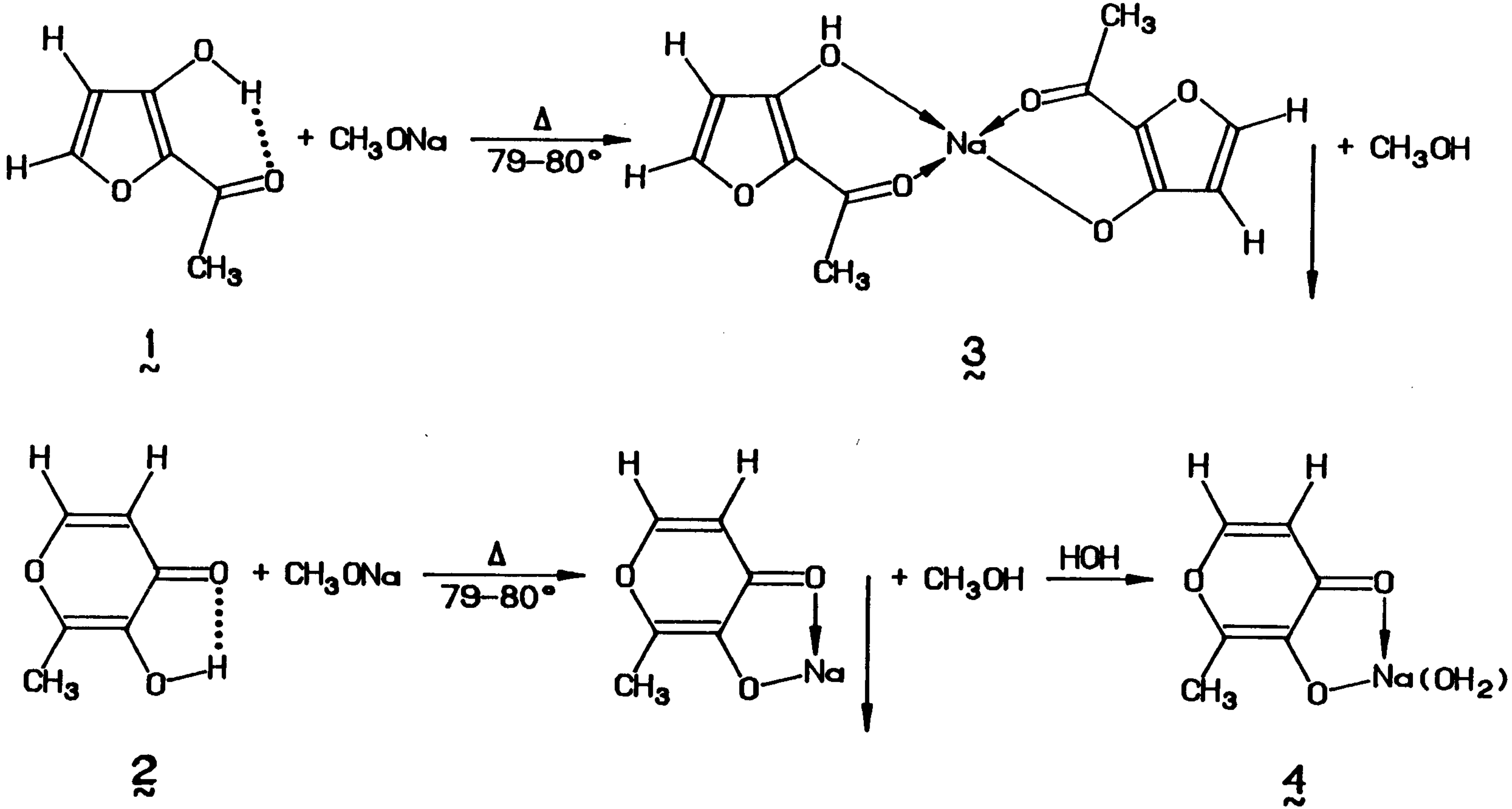
Sidgwick and Plant[5] were the first to demonstrate the existence of coordinated 4-covalent bonded compounds of lithium, sodium, and potassium combined in a 1:2 molecular ratio with Ψ-indoxylspirocyclopentane. Later, Sidgwick and Brewer[6] described sodium bis(salicylaldehyde) as a 4-covalent bonded complex. Brewer[7] extended these observations to rubidium and cesium compounds of salicylaldehyde. Brady and Porter[9] found that 4-isonitroso-1-phenyl-3-methyl-5-pyrazone forms a series of much more stable orange-colored 4-covalent compounds with the alkali metals (Li,Na,K,Rb or Cs) in a 2:1 molar ratio and pointed out that some of these compounds were soluble in chloroform or absolute alcohol.

Rendleman[13] reviewed complexes of alkali and alkaline-earth metals with carbohydrates. Other complexes between various sugars and amides have been reported.[14] Although a copper salt of isomaltol has been reported,[15,16] no complex between sodium and 3-O-hydroxy-2-furyl methyl ketone (isomaltol) (1) or 3-O-hydroxy-2-methyl-4-pyrone (maltol) (2) has been found. This work demonstrates the first known formation, isolation and characterization of a carbohydrate-alkali metal (sodium) 4-covalent bonded chelate of isomaltol (1) and a sodium salt of maltol (2) (with one mole of water).

RESULTS AND DISCUSSION

This investigation resulted from an attempt to condense an aldehyde with an enolic compound, isomaltol (1) (which contains an active methyl group), using sodium alkoxide.

Compound 1 was refluxed in dry benzene, acetone or toluene for 2 min in the presence of an aldehyde. Sodium methoxide[17] was



Scheme 1

added dropwise to the reaction solution. A slightly colored (brown), nonhygroscopic solid precipitated from solution. The separated product was identified as sodium bis(3-O-hydroxy-2-furyl methyl ketone) (3). A 27% yield of compound 3 was obtained after recrystallization from methanol-anhydrous ether. This solid decomposed sharply to a dark liquid at 188-189 °C, and a white crystalline sublimate found in the upper part of the capillary melting-point tube was identified as isomaltol (1). The purified form of compound 3 was found to be soluble in ethanol, methanol and water. Sodium bis(isomaltol) (3) also will release isomaltol (1) when heated overnight in toluene on a steam bath. The resulting toluene-insoluble material (sodium salt of isomaltol) chars without melting when heated, thus behaving as a simple sodium salt which was described previously pertaining to other complexes.[5] The remaining toluene-soluble material melted at 99-101 °C and gave a positive color reaction with ferric chloride reagent; this substance was identified as isomaltol (1). Elemental analyses of compound 3 for C, H and Na agree with a 2:1 molecular ratio for sodium bis(3-O-hydroxy-2-furyl methyl ketone) (3).

Since compound 3 was separated from a reaction mixture containing isomaltol (1) and an aldehyde, two controlled experiments were conducted to determine if the presence of the aldehyde was essential to the formation of compound 3, and to establish that compound 1 did not undergo a rearrangement. Therefore, only isomaltol (1) was treated with sodium methoxide in boiling benzene. Then maltol (2) also was reacted with sodium methoxide under the same conditions. These standardized experiments produced sodium complexes of compounds 1 and 2. The sodium complex of isomaltol (1) decomposed at 188-189 °C, the same decomposition temperature observed for compound 3. The sodium complex of maltol (2), a hydrated sodium salt, sodium 3-O-hydroxy-2-methyl-4-pyrone hydrate (4), charred at 218-223 °C without melting. Compound 4 was also crystallized from methanol-anhydrous ether in a 22% yield. Elemental analyses of the pure solid of compound 4 for C, H, Na and water indicate a compound having one mole of water and a 1:1 molar ratio of maltol (2) to sodium; hence the general structural formulas for sodium bis(3-O-hydroxy-2-furyl methyl ketone) (3) and sodium 3-O-hydroxy-2-methyl-4-pyrone hydrate (4) are as shown in Scheme 1.

After heating and some water loss, compound 4 chars without melting. Therefore, the isolated compound 4 probably interacted with moisture in the air to form a hydrate with one molecule of water, because reactions for both compounds 3 and 4 were carried out under anhydrous conditions.

The IR absorption bands for C=O in compounds 3 (1635 cm^{-1}) and 4 (1750 cm^{-1}) show a large shift relative to the positions of the bands for the parent compounds 1 (1605 cm^{-1}) and 2 (1660 cm^{-1}), a fact that may be attributed to the presence of an enolate ion[18,19,20] in each of the two complexes. Compound 3 ($\Delta_{C=O}$ = 30 cm^{-1}) shows a smaller shift than 4 ($\Delta_{C=O}$ = 90 cm^{-1}), which is probably due to the reduced double-bond character of the carbonyl group for compound 3.[21] A strong, broad absorption band (polymeric type)[21] that extended from 3640-2970 cm^{-1} with a strong shoulder at 3400 cm^{-1} is additional evidence that the sodium salt of maltol (2) is a hydrate.

Crystals of compounds 3 and 4 were submitted for molecular structure determinations by single-crystal x-ray analysis; however, these crystals were too opaque for x-ray studies.

Previously, Hodge and Nelson[16] obtained 3-O-benzoyl-2-furyl methyl ketone in a 56.5% yield when 2 mmoles of compound 1 (0.2 g) was reacted with benzoyl chloride. Under the same conditions 3-O-benzoyl-2-furyl methyl ketone[16] (5) was obtained in a 98.7% yield when 1 mmole of compound 3 (0.2 g) was reacted with benzoyl chloride. This near-quantitative yield is further evidence that the constituents of 3 are combined in a 2:1 molar ratio of compound 1 to sodium, respectively.

EXPERIMENTAL

General methods.—3-O-Hydroxy-2-furyl methyl ketone (1) was obtained by the Hodge and Nelson[16] method. 3-O-Hydroxy-2-methyl-4-pyrone (2) was obtained from John E. Hodge. Sodium methoxide was prepared by the procedure of Renzi et al.[17] Purity of the compounds was established by TLC, melting point (mp) and elemental analyses. TLC was conducted on 0.25 mm of EM Reagent Silica Gel G (Brinkman Instruments, Inc.) with 5% ethanolic sulfuric acid and charring. TLC plates were developed with 75% ethyl acetate-hexane (v/v) for the unsubstituted compounds and with 75% ethyl acetate-methanol for the substituted compounds. ^1H NMR spectra were recorded with a Bruker WH-90 spectrometer: chemical shifts are referred to internal tetramethylsilane. Products were vacuum-dried in the presence of phosphorus pentoxide for 24-48 h at room temperature before analysis. Melting points, measured in capillary tubes, are not corrected. Infrared spectra were determined in potassium bromide pellets (1.22 mm thick; 0.1 M concentration) with a Perkin-Elmer Model 621 spectrophotometer. Microchemical analyses were performed by the Galbraith Laboratories, Inc., P.O. Box 4187, 2323 Sycamore Drive, Knoxville, TN 37921.

Sodium bis(3-O-hydroxy-2-furyl methyl ketone) (3).—3-O-Hydroxy-2-furyl methyl ketone (1) (1.7 g; 0.014 mole) was dissolved in dry benzene (100 mL), acetone or toluene under reflux for 2 min. Sodium methoxide[17] (2 mL, .0044 mole) was added dropwise. As compound 3 formed, it was separated by precipitation from the solution. The reaction was allowed to reflux for 2.5 h. Compound 3 was crystallized from reagent grade methanol-anhydrous ether in 27% yield (1.0 g): mp 188-189 °C; soluble in ethanol, methanol, and water; ^1H NMR (methanol-d_4): δ 2.36 (singlet, acetoxy methyl), δ 6.096 and 6.119, J = 2.05 Hz (doublet, vinyl proton), δ 7.478 and 7.501, J = 2.07 Hz (doublet, vinyl proton); ν_{max} 1635 cm^{-1} (C=O), 1595, 1535, 1478, and 1425 cm^{-1} (C=C).

Anal. Calcd for $C_{12}H_{11}NaO_6$: %C, 52.56; H, 4.04; Na, 8.39. Found: %C, 52.60; H, 4.2; Na, 8.47.

Sodium 3-O-hydroxy-2-methyl-4-pyrone hydrate (4).—Compound 2 (1.7 g; 0.014 mole) was reacted with sodium methoxide[17] under the same conditions as for compound (1), which produced 4. As compound 4 was formed, it precipitated from the reaction mixture. A 22% yield (0.46 g) was obtained after recrystallization from reagent grade methanol-anhydrous ether. The solid charred without melting at 218-223 °C; hygroscopic; soluble in ethanol, methanol and water. ^1H NMR (methanol-d_4): δ 2.35 (singlet, methyl protons), δ 6.285 and 6.344, J = 5.29 Hz (doublet, vinyl proton), δ 7.741

and 7.800, J = 5.32 Hz (doublet, vinyl proton); ν_{max} 1750 cm^{-1} (C=O), 1625 cm^{-1} (C=C, unconjugated or conjugated[21]), 1575, 1560, 1515, and 1455 cm^{-1} (C=C), 3640-2970 cm^{-1} (strong broad polymeric type[21]), 3400 cm^{-1} (strong shoulder).

Anal. Calcd for $C_6H_5NaO_3 \cdot H_2O$: %C, 43.40; H, 4.25; Na, 13.84; HOH, 10.84. Found: %C, 43.20; H, 4.44; Na, 13.63; HOH, 10.95.

3-O-Benzoyl-2-furyl methyl ketone (5).—The O-benzoyl ester (5) was prepared from compound 3 (0.2 g) by the procedure of Hodge and Nelson[16] in 98.7% yield (0.227 g), whereby their method gave a 56.5% yield: mp 98.5-100 °C; reported[15] 99 °C; reported[16] 100-101 °C; ^1H NMR (chloroform-d): δ 2.502 (singlet, acetoxy methyl), δ 6.845 and 6.867, J = 1.99 Hz (doublet, vinyl proton), δ 7.502 and 7.524, J = 1.95 Hz (doublet, vinyl proton) δ 7.591 (complex multiplets, aromatic protons), δ 8.161 (complex multiplets, aromatic protons); ν_{max} 1755 cm^{-1} (ester absorption), 1664 (C=O), 1595, 1490, 1458, 1440, and 1420 (C=C).

Anal. Calcd for $C_{13}H_{10}O_4$: %C, 67.80; H, 4.38. Found: %C, 68.15; H, 4.42.

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