ACTA CHEMICA SCANDINAVICA 10 (1956) 1097—1099

Isolation of N-[D-2,3-Dihydroxy-*n*-propyl]-taurine from *Gigartina leptorhynchos*

BÖRJE WICKBERG

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

In an investigation of the red alga *Gigartina leptorhynchos* a new internal salt was isolated. This was shown to be N-[D-2,3-dihydroxy-*n*-propyl]-taurine, for which the shorter name D-glyceryltaurine is suggested. Taurine, floridoside, glycerol and small amounts of *meso*-inositol, mytilitol and laminitol were also found.

In previous communications from this institute investigations on the occurrence of internal salts [1] and of low-molecular weight carbohydrates [2] in various algae have been reported. The present paper records the investigation of the red alga *Gigartina leptorhynchos*, *Florideae*, order *Gigartinales*, from which a new internal salt, shown to be N-[D-2,3-dihydroxy-*n*-propyl]-taurine or shortly, D-glyceryltaurine, was isolated. In addition taurine, floridoside, glycerol and small amounts of the cyclitols *meso*-inositol, laminitol and mytilitol were found.

Floridoside is a common constituent of algae belonging to *Florideae* while taurine and its N-methyl derivatives [1] are frequently met with throughout the red algae. The amounts of cyclitols found, being of the order 0.001 %, are so small that these substances could possibly derive from impurities in the material investigated.

The new internal salt was optically active $[\alpha]_D^{23}$ −21° (water) and had a much lower melting point (163.5—164.5°) than taurine and its N-methyl derivatives which all melt in the range 240—340°. On a carbon column the new compound travels at about the rate of a hexitol which is much slower than the rate observed for the other taurines. When paper chromatograms were run in ethyl acetate-acetic acid-water (3:1:1) the R_F-value of the substance was some 10 % higher than for taurine. On the chromatogram the substance could be detected with the silver nitrate-sodium ethoxide reagent and with ninhydrin. With the latter reagent rather strong heating was required and the colour produced was fainter than that observed with taurine, a behaviour which is similar to that of N-methyl taurine. The crude compound could be freed from

carbohydrates by adsorption on Amberlite resin IR 400 in the OH-state and subsequent elution with dilute acetic acid.

Analysis was in fair agreement with the composition $C_5H_{13}O_5NS$, and no solvent of crystallisation was detected. The substance was unaffected by hydrolysis in 2 N HCl for 15 h at 120°. Periodate oxidations indicated a consumption of 2 moles of oxidant with the formation of 2 moles of formaldehyde. From the oxidized material pure taurine was isolated. According to these facts the compound should have structure I. This conclusion was confirmed by the synthesis of D-glyceryl-taurine by reductive coupling of *iso*-propylidene-D-glyceric aldehyde with taurine and subsequent hydrolysis of the *iso*propylidene derivative obtained. The optical rotation, melting point and chromatographic behaviour were the same for the synthetic product as for the substance obtained from the alga, and the mixed melting point for the two preparations showed no depression. The internal salt from the alga thus possesses the D-form of structure I.

$H_3\overset{+}{N}CH_2CH_2SO_3^-$
CH_2
$CH(OH)$
CH_2OH

I. Glyceryltaurine

EXPERIMENTAL

The alga (320 g) was extracted with ether for 2 days and with methanol for 14 days. The methanol extract was concentrated to a syrup which was stirred with water, the mixture was filtered and the filtrate de-ionised with Amberlite IR 120 and IR 4B and concentrated to dryness. The residue (5.5 g) was dissolved in water (100 ml) and the solution added to the top of a carbon-Celite column (35 × 4.5 cm). The column was eluted with water (2 000 ml) and then with aqueous ethanol (4 000 ml) the concentration of which was linearly raised from 0 to 30 %. The eluate was fractionated and investigated by paper chromatography using as solvent ethyl acetate-acetic acid-water. The main fractions were de-ionised as before and concentrated to dryness.

Fraction No. 1 (200 mg) contained only one component and this was ninhydrin-positive. After recrystallisation from aqueous ethanol taurine (150 mg) was obtained, m. p. 320—8° * alone or admixed with an authentic sample.

Fraction No. 2 (112 mg) contained two components with the same R_F-values as *meso*-inositol and glycerol. Separation on Whatman filter paper No. 3 MM yielded *meso*-inositol (15 mg) which after recrystallisation had m. p. 222—225°, alone or admixed with authentic material. The glycerol fraction (90 mg) was benzoylated by the Schotten-Bauman procedure, yielding a benzoate (110 mg) which melted at 74—75° and gave no melting point depression with authentic glycerol tribenzoate.

Fraction No. 3 (30 mg) gave one reducing spot. Recrystallisation and acetylation yielded an acetate which crystallised in needles melting at 170—172° with simultaneous transformation into rhombic crystals melting at 184—186°. The melting points were undepressed on admixture with mytilitol hexa-acetate.

Fraction No. 4 gave a spot indistinguishable from that of laminitol. Recrystallisation yielded a substance (15 mg) a sample of which was acetylated yielding an acetate, m. p. 155—157° alone or admixed with an authentic sample of laminitol hexa-acetate.

Fraction No. 5 (580 mg) contained a substance which gave one strong spot with the silver nitrate and the ninhydrin reagents. It was adsorbed on the Amberlite resin IR 400 in OH-form and subsequently eluted with 5 % aqueous acetic acid. The crude crystalline material so obtained (420 mg) melted when heated under aqueous ethanol and was recrystallised by the careful addition of ethanol to its slightly warmed aqueous solution. M. p. 163.5—164.5°, $[\alpha]_D^{23}$ −21° (water, c = 2.0). (Found: C 30.4; H 6.68; N 6.64; S 14.7. Calc. for $C_5H_{13}O_5NS$: C 30.1; H 6.58; N 7.03; S 16.1.)

* All melting points are corrected.

Fraction No. 6 (2.3 g) contained a substance which was recrystallised from aqueous ethanol. M. p. 125—128°, $[\alpha]_D^{23}$ +152° (water, c = 2). These data and its chromatographic behaviour showed it to be floridoside.

Periodate oxidations of the internal salt from fraction 5. Periodate oxidations were carried out on a micro scale with an aqueous solution containing *ca.* 2 mg/ml of the internal salt from fraction 5.

a) *Periodate consumption.* To each sample (0.5 ml) 0.03 molar sodium metaperiodate solution (1 ml) was added. After varying times saturated sodium bicarbonate solution (1 ml), 0.1 N sodium arsenite (1 ml) and 20 % aqueous potassium iodide (0.2 ml) were added and after standing for 15 minutes the mixture was titrated with 0.02 N standard iodine solution. Within a few minutes the periodate consumed was 2.1 moles/mole substance and this value rose to 2.2 moles overnight.

b) *Formation of formaldehyde and taurine.* The sample (2 ml) was oxidized with sodium periodate and the formaldehyde formed was determined as its dimedone compound as described by Reeves [3]. The dimedone compound had m. p. 193—194°, alone or admixed with an authentic sample and the yield corresponded to the formation of 1.9 moles of formaldehyde per mole of internal salt.

The mother liquors from the dimedone precipitation were freed from excess dimedone by extraction with ether and from inorganic salts by passing the solution through Amberlite resins IR 120 and IR 4B. By evaporation of the de-ionised solution and subsequent recrystallisations from dilute methanol, pure taurine was obtained, m. p. 325—329°, alone or mixed with authentic material.

D-*Glyceryltaurine. Iso*propylidene-D-glyceric aldehyde was prepared from D-mannitol as described by Baer [4,5].

To a solution of freshly distilled *iso*propylidene-D-glyceric aldehyde (6.4 mmole, 0.83 g) and taurine (8 mmole, 1.0 g) in water (10 ml) colloidal platinum solution [6] (4 ml, 8 mg Pt) was added and the mixture shaken with hydrogen for 100 hours at room temperature and atmospheric pressure. The hydrogen uptake was 7.9 mmole. This high value may have been due to the reduction of liberated acetone, as the hydrogenated mixture was found to be slightly acid afterwards.

After hydrogenation the mixture was heated for a short while with a minute amount of hydrochloric acid to remove *iso*propylidene groups, filtered through a small amount of carbon-Celite and the filtrate concentrated and added to the top of a carbon-Celite column (170 ml carbon-Celite 1:1). The column was subjected to gradient elution (2 000 ml, 0—30 % ethanol); the appropriate fractions of the eluate were concentrated to dryness and the residue (0.9 g) was after treatment with Amberlite resins IR 120 and IR 4B recrystallised from dilute ethanol yielding a product (0.67 g, 53 % calc. on *iso*propylidene-D-glyceric aldehyde) which proved to be identical with the internal salt isolated from the alga. M. p. 163—164.5° alone or mixed with the natural product, $[\alpha]_D^{23}$ −19° (water, c = 2), CH_2O formed upon periodate oxidation: 2 moles/mole comp.

Acknowledgements. The author is indebted to *Statens Naturvetenskapliga Forskningsråd* for financial support and to Ing. L. Mikiver for his skilful assistance. The alga was kindly supplied by Dr. Colm O'h Eocha, University of California.

REFERENCES

1. Lindberg, B. *Acta Chem. Scand.* **9** (1955) 1323.
2. Lindberg, B. *Acta Chem. Scand.* **9** (1955) 1097.
3. Reeves, R. E. *J. Am. Chem. Soc.* **63** (1941) 1476.
4. Baer, E. *J. Am. Chem. Soc.* **67** (1945) 338.
5. Baer, E. and Fischer, H. O. L. *J. Biol. Chem.* **128** (1939) 463.
6. Skita, A. and Meyer, W. A. *Ber.* **45** (1912) 3580.

Received May 5, 1956.