Tetrahedron Letters No. 4, pp. 1-4, 1960. Pergamon Press Ltd. Printed in Great Britain.

SIPHULIN, A CHROMANONE TYPE LICHEN ACID

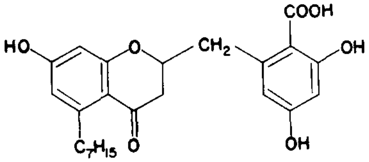
T. Bruun

Institutt for Organisk Kjemi, Norges Tekniske Högskole

Trondheim, Norway

(Received 18 January 1960)

SIPHULA ceratites (Fr.) Th. Fr., an imperfect lichen with a disjunctive distribution in Norway, contains a new type of carboxylic acid for which the name siphulin and the constitution 7-hydroxy-5-n-heptyl-2 [3', 5'-dihydroxy-2-carboxybenzyl] - chroman-4-one (I) are proposed.



I

The acid melted at about 180° with evolution of carbon dioxide (Found: C, 67.7; H, 6.45. $C_{24}H_{28}O_7$ requires C, 67.3; H, 6.6%). Potentiometric titration in ethanol-water (3:2) indicated an equivalent weight of 425 (required M.W.-428). It contained no methoxyl group. The acid was optically inactive, and this was confirmed by optical rotatory dispersion measurements, very kindly carried out by Dr. W. Klyne, London, England. U.V. absorption λ_{max} 2440, 2510, 2635 and 2935, ε 29,500, 30,000, 20,500, 23,500 respectively,

λ_{min} 2410, 2480, 2585 and 2470 Å, ε 29,900, 27,500, 19,500 and 17,500. The infra-red spectrum in KBr gave no information apart from an indication that the substance might be an o-hydroxy carboxylic acid since it contained a very broad, indistinct band at about 1650 - 1660 cm^{-1}.

The acid was characterized by the preparation of a tri-acetate a methyl ester, a dimethoxy methyl ester, a methyl ester tri-acetate, a dimethoxy methyl ester acetate and a trimethoxy methyl ester. Of these the last three substances gave information of the presence of a carbonyl function inert towards the usual carbonyl reagents, as exemplified by the trimethoxy methyl ester: m.p. 77-78° (Found: C, 70.1; H, 7.2; O-Me, 26.5. $C_{28}H_{36}O_7$ requires C, 70.0; H, 7.55; O-Me 25.8%). λ_{max} 2500 and 2860 Å, ε 25,500 and 20,500, respectively, with an inflexion at about 2400 Å, ε 31,000 and λ_{min} at 2490 and 2620 Å, ε 25,000 and 11,500. The infra-red spectrum showed bands at 1730 cm^{-1} (ester) and at 1655 cm^{-1} (conjugated carbonyl group). This trimethoxy methyl ester with N-bromo-succinimide furnished a monobromo compound, m.p. 123-125° (Found: C, 59.7, 59.85; H, 5.9, 6.0; Br, 14.1, 13.9; O-Me, 21.6, 20.4, 20.4; C-Me 3.0, 4.2. $C_{28}H_{35}BrO_7$ requires C, 59.7; H, 6.25; Br, 14.2; O-Me, 22.0; C-Me, 2.65%). λ_{max} 2505 and 2900 Å, ε 24,500 and 20,500, respectively, λ_{min} 2485 and 2610 Å, ε 24,000 and 16,500. The infra-red spectrum showed carbonyl bands at 1730 and 1655 cm^{-1} with a should at about 1670 cm^{-1}.

Alkaline degradation of the acid gave as isolated and identified compounds sphaerophorol (3,5-dihydroxy-n-heptyl-benzene), m.p. 56-57°, 3,5-dihydroxyphenylacetic acid, m.p. 126-127° (anhydrous) and acetic acid (p-bromophenacyl ester, m.p. 85-86°).

Alkaline degradation of the trimethoxy methyl ester afforded, apart from products with no direct bearing on the constitutional problem, 2-carboxy-3,5-dimethoxyphenylacetic acid, m.p. 174-175°, λ_{max} 2505 and 2835 Å, ε 6100 and 3500, λ_{min} 2370 and 2705 Å, ε 5200 and 2300, a band in the infra-red at 1720 cm^{-1} with a shoulder at 1680 cm^{-1}; and a liquid compound, presumably 2-hydroxy-4-methoxy-6-n-heptylacetophenone, b.p. $110^{o}/10^{-3}$ mm (bath), n_D^{19} 1.5339, bluish-violet colour with ferric chloride (Found: C, 72.8; H, 9.1; O-Me, 11.8; C-Me, 10.5. $C_{16}H_{24}O_3$ requires C, 72.7; H, 9.15; O-Me, 11.7; C-Me, 11.4%), λ_{max} 2700 Å, ε 7000, λ_{min} 2460 Å, ε 3300; a broad band in the infra-red at about 1690 cm^{-1} (liq.).

Oxidation of the trimethoxy methyl ester with selenium dioxide furnished a lactone, m.p. 167-168° (Found: C, 67.1; H, 6.2; O-Me, 19.25. $C_{27}H_{32}O_8$ requires C, 66.9; H, 6.65; O-Me, 19.2%), λ_{max} 2540 and 2960 Å, ε 29,500 and 22,000, λ_{infl} at about 2440 and 2620 Å, ε 29,500 and 19,500, λ_{min} 2500 and 2740 Å, ε 27,000 and 14,000 carbonyl bands in the infra-red at 1772 and 1652 cm^{-1}.

Potassium permanganate oxidation of the lactone afforded 3,5-dimethoxyphthalic acid, identified as the anhydride, m.p. 149-150°, and 2-hydroxy-4-methoxy-6-n-heptylbenzoic acid, m.p. 125-126° (Found: C, 67.4; H, 8.3. $C_{15}H_{22}O_4$ requires C, 67.65; H, 8.35%). λ_{max} at 2175, 2605 and 3020 Å, ε 32,500, 15,000 and 6000, λ_{min} at 2365 and 2800 Å, ε 4400 and 2400, carbonyl band at 1652 cm^{-1} (KBr).

All identifications were secured by comparison of m.p., mixed m.p., u.v. and i.r. spectra with corresponding data for authentic (below) compounds. All ultra-violet absorption spectra were measured in solutions in ethanol on a Perkin-Elmer No. 13 spectrometer, and infra-red spectra on a Perkin-Elmer No. 21 spectrometer.

2-Hydroxy-4-methoxy-6-neheptylbenzoic acid was synthesized from sphaerophoral carboxylic acid, prepared by careful hydrolysis of sphaerophorin by prolonged action of diazomethane followed by saponification. 3,5-dihydroxyphenylacetic acid was synthesized according to Theilacker and Schmid[2] and the p-bromophenacyl ester of acetic acid by the standard method of phenacyl esters. 2-Carboxy-3,5-dimethoxyphenylacetic acid was synthesized from ethyl 3,5-dihydroxy-2-carbethoxyphenylacetate[3] as starting material.

The potentiometric titration was carried out by Mrs. A. R. Alertsen.

Acknowledgements - Thank are due to Professor S. Shibata, Tokyo, Japan, for providing the comparison specimen of sphaerophorol and a sample of sphaerophorin, to Dr. C.A. Wachtmeister, Stockholm, for another sample of sphaerophorin, and to Dr. A.I. Scott, Glasgow, for a sample of 3,5-dimethoxyphthalic acid.

The author also wishes to thank Professor N.A. Sorensen for his interest and assistance in collecting material.

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