a convenient source for the synthesis of potassium 3,4-*o*-isopropylidene-L-threonate[3] and of threonic acid, although L-threonic acid can also be obtained in equimolecular mixture with oxalic acid from the direct oxidation of L-ascorbic acid[4,5]. There is increasing interest in L-threonic acid, because it is a possible intermediate in the catabolism of L-ascorbic acid *in vivo*.

	Number	mg substance	mg H_2O	mg CO_2	% H	% C
Ascorbic acid	1C 6	5.861	2.360	8.810	4.51	41.02
Small-scale run	1C 9S	4.619	2.340	8.500	5.67	50.21
Large-scale run	2C 9L	4.940	2.505	9.070	5.68	50.10
Large-scale run, recrystallized	3C 9R	5.176	2.655	9.530	5.74	50.24

Dry hydrogen chloride is rapidly bubbled through glass tubing of 8 mm I.D. for 5 min into a 200 ml centrifuge flask containing 10 g (0.057 mole) of powdered L-ascorbic acid and 100 ml of dry, redistilled acetone. After addition of 80 ml *n*-hexane, stirring, cooling in ice water and centrifuging, the supernate is decanted. The precipitate is washed four times with 140 ml of acetone-hexane mixture 4:7 (v/v), with stirring, cooling, centrifuging and removal of supernate after each addition. The flask is closed with a rubber cap, and opened only for minimal periods required for the operations. The yield of 5,6-*o*-isopropylidene-L-ascorbic acid, dried *in vacuo* over sodium hydroxide, is 85–90%, m.p. 219–222° (cor., dec.). Less than 2 h are required for all steps up to the drying process. Thoroughly powdered starting material is essential, because admixture of fairly large crystals sometimes gives product having depressed melting point, i.e. presumably contains unreacted L-ascorbic acid. The unrecrystallized material is substantially pure, judged by its melting point, mixed melting point with isopropylidene derivative prepared by use of anhydrous copper sulfate[2] and analysis. It may be recrystallized from acetone-hexane mixture. Alternatively, it may be washed with peroxide-free diethyl ether, dried *in vacuo* and then continuously extracted with dry, peroxide-free diethyl ether to yield crystalline 5,6-*o*-isopropylidene-L-ascorbic acid in the receiving flask, with a melting point at 223-224° (cor., dec.), slightly higher and better defined than that reported by V. VARGHA[2]. Using glass-stoppered test tubes and appropriate quantities of solvents and reagents, similar yields may be obtained from 1 mmole of L-ascorbic acid. The procedure is thus also useful for preparing labelled threonic acid[3].

Zusammenfassung. Die Synthese der 5,6-*o*-Isopropyliden-L-ascorbinsäure mit Hilfe von Chlorwasserstoffgas wird beschrieben.

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August 27, 1963.

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The Nature of Carbonate Contents in Tooth Mineral[1]

Precipitation experiments *in vitro* from aqueous solutions demonstrate that in the pure calcium phosphate system no ideal crystallization processes will arise, but we must consider these precipitations as agglomerations of calcium phosphate complexes (colloid clusters, 0.005–0.05 μm, with positive excess charge).

This situation, found during development of teeth, is complicated by the presence of mucous substances as well as by additional carbonate, citrate and other ions. Hereby, the amorphous character of a precipitated matter would be likewise favoured and yields a matrix gel.

The regular formation of the apatitic enamel crystals will be performed by the combination of the following events: the fluoride content and the pattern of keratine. The one effect inducing the apatitic structure, even of small amounts of fluoride ions, will be caused by the primary formation of fluorapatite germs[2]. The function of the keratine structure as epitactic matrix effects the parallel straightened inotrope texture and the longitudinal extension of the enamel crystals[3].

The difference between the solubility of the crystallized apatite and the amorphical matrix gel enables a recrystallization of the enamel matter. In this gel the main part of the carbonate ions will be bound chemically and there deposited. The carbonate (fluoride etc.) is therefore available as ion only at the absolute extent of solubility – that is at small concentrations – for combining with the crystal bindings of the enamel crystals. This slow building process determines an orderly separation of the crystalline phase[4]. At larger concentrations, carbonate and phosphate mutually disturb the regular crystallization of their low solubility calcium compounds[5] and are not suited for the corresponding isomorphous substitution in their lattice formations. It is supposed that, in topochemical reactions, the apatite lattice will be able to take up a small percentage (< 2%) of carbonate ions[6]. Herewith vacancies occur, which must be neutralized in their charges. With regard to the structure of the lattice, the carbonate uptake is always followed by a contraction of the elementary unit along a. We can ascertain that the answer to the question on the nature of the carbonate in the tooth material cannot be given by deciding whether the carbonate is an integral part of the dental apatite structure or not.

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Carbonate apatite structure of tooth means more or less a close approximation to the biological reality: besides carbonate further elements are present: F, Cl, SO_4; Na, K, Mg—also there is the close relation to the protein pattern—whose influences to the lattice combination is too complex to perceive an additive dependence on one of these ions. We should not go further now than stating that enamel crystals have the structure of an apatite which is partly substituted by carbonate, fluoride, chloride etc. and which crystallizes according to the type of the often tested hydroxyapatite.

I want to point out, however, that the mineral substance of the tooth is to be considered as a paracrystalline apatitic texture. This means that, besides the well ordered crystalline regions, heavily faulty ordered and amorphous mineral ranges are present, which do not differ in their qualitative chemical composition but show fluctuations in their stoichiometric combinations. This paracrystalline structure is necessarily involved in the chemical conditions of the mechanism of the tooth mineralization.

Zusammenfassung. Der Aufbau der Zahnhartsubstanz ist im Verlaufe ihrer Bildung durch mehrere Faktoren – u.a. Begleitionen, Texturvorlage (Proteinmatrix) – bestimmt. Der Einfluss des Carbonatgehalts wurde in diesem Zusammenhang besonders im Hinblick auf dessen kristallchemische Funktion bei der Zahnmineralisation (parakristalline Struktur des teilweise isomorph substituierten Apatits) untersucht.

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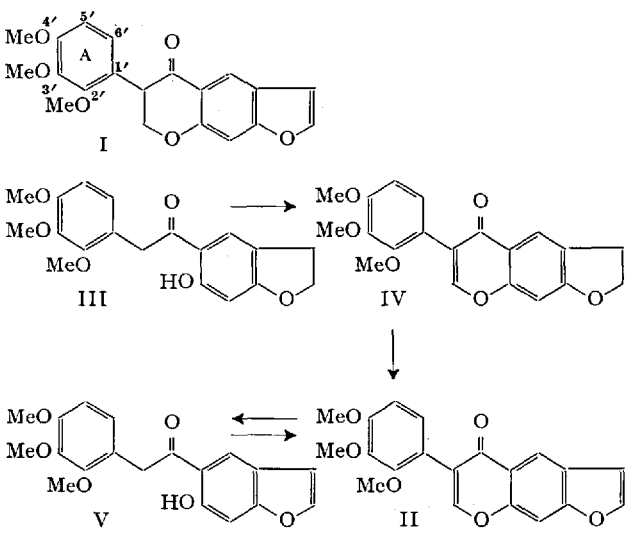
Forschungsgruppe für Mikromorphologie im Fritz-Haber-Institut (Max-Planck-Gesellschaft), Berlin-Dahlem (Deutschland), 5. August 1963.

Structure of Nepseudin. Synthesis of Dehydronepseudin

Nepseudin has recently been isolated along with neotenone, dolineone, and pachyrrhizin from the root of the leguminous plant *Neorautanenia pseudopachyrrhiza*[1]. As a result of degradative experiments, nepseudin has been shown to be the furanoisoflavanone (I) similar to neotenone but with a unique 2′, 3′, 4′-trimethoxylated ring A replacing the normal 2′, 4′, 5′-oxygenation pattern. On dehydrogenation with manganese dioxide, (I) has been converted into dehydronepseudin, the furanoisoflavone (II). We wish to report the total synthesis of (II) confirming the proposed structures.

Hoesch condensation of 6-hydroxy-2, 3-dihydrobenzo[b]furan[2] with 2, 3, 4-trimethoxybenzyl cyanide[3] yielded 6-hydroxy-5-(2, 3, 4-trimethoxyphenylacetyl)-2, 3-dihydrobenzo[b]furan (III, m.p. 129° ~130°, IR 1637 cm^{-1} (Nujol) (CO). Found: C, 66.37; H, 5.99. $C_{19}H_{20}O_6$ requires: C, 66.27; H, 5.85%). Treatment of (III) with ethyl orthoformate-pyridine-piperidine gave the dihydro compound (IV m. p. 143° ~144°, IR 1628 cm^{-1} (Nujol) (CO). Found: C, 67.87; H, 5.22. $C_{20}H_{18}O_6$ requires: C, 67.79; H, 5.12%) of (II). On dehydrogenation with N-bromosuccinimide (IV) afforded dehydronepseudin (II, m.p. 164° ~165°, IR 1649 cm^{-1} (Nujol) (CO), UV λ_{max}^{EtOH} mμ (log ε); 244 (4.59), 324 (3.86). Found: C, 67.96; H, 4.61. $C_{20}H_{16}O_6$ requires: C, 68.18; H, 4.58%)(lit.[1], m.p. 158° ~160°, IR 1647cm^{-1} (Nujol) (CO), UV λ_{max}^{EtOH} mμ (log ε); 245 (4.64), 325 (3.92)). On alkaline hydrolysis (II) gave 6-hydroxy-5-(2, 3, 4-trimethoxyphenylacetyl)benzo[b]furan[1] (V, m.p. 118°, IR 1639 cm^{-1} (Nujol) (CO), UV λ_{max}^{EtOH} mμ (log ε); 236 (4.76), 258.5 (4.07), 272.5 (3.97), 345 (3.71). Found: C, 66.69; H, 5.40. $C_{19}H_{18}O_6$ requires: C, 66.66; H, 5.30%) (lit.[1], m.p. 118° ~119°, IR 1645 cm^{-1} (Nujol) (CO), UV λ_{max}^{EtOH} mμ (log ε); 235 (4.66), 258 (4.00), 270 (3.86), 345 (3.60)). The parent isoflavone (II) could be reconstructed by treating (V) with ethyl orthoformate-pyridine-piperidine. On the basis of these syntheses the structure of (I) for nepseudin would be reasonably explained.



Zusammenfassung. Die Konstitution (I) für Nepseudin wird durch die Synthese des Dehydronepseudins (II), das aus 6-Oxy-2, 3-dihydrobenzo[b]furan und 2, 3, 4-Trimethoxyphenylessigsäurenitril in drei Reaktionsstufen erhalten wird, aufgeklärt.

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