

Note

The isolation of perseitol and volemitol from *Sedum*, and some other observations on *Sedum* constituents

NELSON K. RICHTMYER

National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Md. 20014 (U. S. A.)

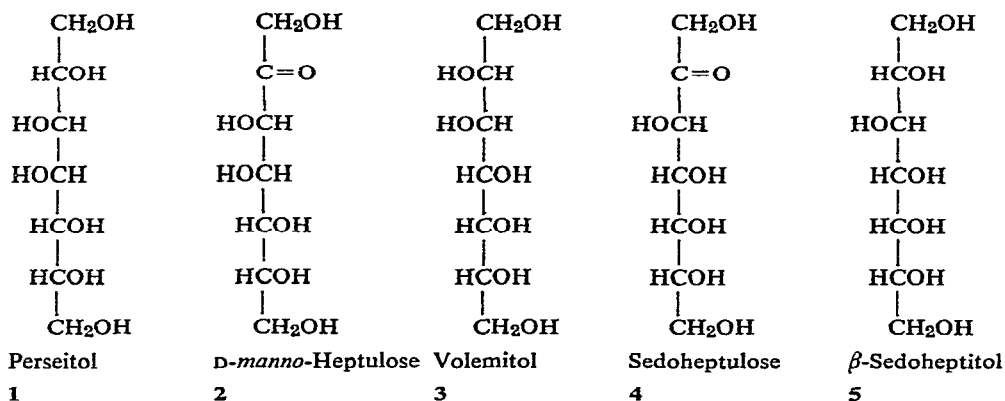
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The preceding paper¹ discussed the occurrence, in plants, of D-manno-heptulose (2) and sedoheptulose (D-althro-heptulose, 4), and of the heptitols that are closely related to them by reduction, namely, perseitol (D-glycero-D-galacto-heptitol, 1), volemitol (D-glycero-D-manno-heptitol, 3), and β -sedoheptitol (D-glycero-D-gluco-heptitol, 5). For example, compounds 1, 2, and 3 have been isolated from the avocado¹ (family, Lauraceae) and compounds 2, 3, 4, and 5 from *Primula officinalis* Jacq.² (family, Primulaceae). The present paper describes the isolation from *Sedum* species (family, Crassulaceae) of perseitol (1) and volemitol (3), in addition to sedoheptulose (4, as the crystalline anhydride sedoheptulosan) and β -sedoheptitol (5), whose isolation from *Sedum* has been reported earlier³. Thus, it is seen that D-manno-heptulose (2) in the avocado is accompanied by heptitols 1 and 3, and that sedoheptulose (4) in *Primula* and *Sedum* is accompanied by heptitols 3 and 5. Inasmuch as D-manno-heptulose (2) and sedoheptulose (4) occur together in some plants, such as *Primula*, it is logical to predict that, eventually, all five of these compounds will be isolated from the same plant extract.

As a result of the earlier part of this investigation, Charlson and Richtmyer³ reported the isolation from *Sedum* (as well as from the avocado) of D-glycero-D-manno-octulose. Subsequently, Sephton and Richtmyer⁴ isolated, also, D-glycero-L-galacto-octulose, D-erythro-L-gluco-nonulose, and D-erythro-L-galacto-nonulose from the avocado; they proved the structure of, and synthesized, each of the last three higher-carbon sugars. Begbie and Richtmyer² isolated from *Primula* roots, and independently proved the structure of, each of the two octuloses and two nonuloses. Because these investigations^{2,4} were so thorough, it no longer seems important to continue with the tedious separation, purification, and identification of the other 8- and 9-carbon ketoses in *Sedum*, and work on the problem has been abandoned.

Because D-erythro-D-galacto-octitol is closely related to D-glycero-D-manno-octulose and both have been found in the avocado³, and because that octulose has been found also in *Sedum*³, a special search was made for the octitol in *Sedum*. To this end, 37.5 kg of *S. spectabile* Bor. was processed as described in the Experimental section, and finally fractionated on a column of Dowex 50W-X8 (Ba²⁺) ion-exchange

resin; no more than a trace, if any, of the octitol could be detected by paper chromatography.



EXPERIMENTAL

Further fractionation of Sedum extract. — In 1960, Charlson and Richtmyer³ described (a) the extraction of 385 kg of *Sedum* plants (principally *S. spectabile*) with water, and (b) subsequent treatments of the extract with methanol to precipitate gums, with yeast to remove fermentable sugars, with dilute acid to convert sedoheptulose into sedoheptulosan (of which 2.4 kg was isolated), and with bromine water to decompose the aldoses. The resulting product was 345 g of syrup that contained at least a dozen ketoses, their anhydrides, and polyhydric alcohols. This material was fractionated on cellulose columns by eluting with mixtures of benzene and methanol containing 1% of water. The eluate was divided into eleven fractions and, as described earlier³, from a 3.6-g portion of fraction 9 were separated D-glycero-D-manno-octulose and β-sedoheptitol. The remainder of fractions 8–11 weighed 33.5 g, and a description of its further investigation was promised.

That investigation was started by putting the 33.5 g of syrup that contained the octulose and nonulose portions of the extract on a column of cellulose (55 × 7.5 cm) and eluting with ethyl acetate–acetic acid–water (from 36:5:4 to 3:1:1). The octulose fraction (as determined by paper chromatography) was set aside, and the nonulose fraction was heated with 0.2M aqueous hydrochloric acid to hydrolyze a compound that appeared to be a sedoheptulose-containing disaccharide. After being deionized and concentrated, this material (16 g) was then refractionated on a cellulose column by eluting with aqueous butyl alcohol, to yield an additional octulose fraction. At this point, the octulose fractions were combined (6.2 g), put on top of a new cellulose column (88 × 5 cm), and eluted with quarter-saturated aqueous butyl alcohol. After 7090 ml of eluate had been separated as a forerun, the use of an automatic fraction-collector was begun, and 16-ml fractions were collected. These fractions were combined, and concentrated, in groups of 25; crystalline material was deposited in some of the combined fractions.

Fractions 551–950 yielded 0.84 g of crystals that were recrystallized twice from methanol containing a few drops of water. The product thus obtained (0.20 g of needles) melted at 150–152° and was identified as **volemitol (3)** by a mixed m.p. of 151–152° (the authentic volemitol melted at 152–153°) and by comparison of its i.r. spectrum (Nujol mull) with that of authentic volemitol. The mother liquor from the volemitol began to crystallize spontaneously, and deposited **β -sedoheptitol (5)** which was identified by m.p. and mixed m.p. of 128–130°.

Fractions 1951–2575 yielded 22 mg of crystals. These were recrystallized from aqueous methanol, in clusters of small, elongated prisms. A melting point and mixed m.p. of 187–188°, together with a comparison of i.r. spectra, identified the product as **perseitol (1)**.

A search for D-erythro-D-galacto-octitol in Sedum spectabile. — A quantity (77.2 kg) of *S. spectabile* was extracted with water; the extract was concentrated, and poured into methanol; the mixture was filtered, and the filtrate was concentrated, deionized with Amberlite IR-120 and Duolite A-4 ion-exchange resins, and evaporated to yield 600 g of syrup. An aqueous solution of this syrup in a stainless-steel pot was heated for 32 h on a steam bath with a total of 750 g of barium hydroxide octahydrate to maintain alkalinity (to decompose all reducing sugars). The solution was made neutral with carbon dioxide, the suspension filtered, and the filtrate deionized with Amberlite IR-120 and Duolite A-4 ion-exchange resins, and finally with Amberlite IRA-400 (to remove any resistant lactones). Evaporation of the solution gave 30 g of syrup that showed 6 heavy spots and 4 light spots on paper chromatograms (6:4:3 butyl alcohol–pyridine–water; visualized with ammoniacal silver nitrate at room temperature). Crystallization began spontaneously in the syrup, and was aided by the addition of methanol and cooling. The first crop weighed 2.0 g and, after recrystallization from aqueous methanol, gave 1.8 g of *myo*-inositol having m.p. and mixed m.p. of 224–225°. The mother liquor from the first crop was concentrated in a current of air to yield, spontaneously, a second crop of crystals that weighed 13.5 g; recrystallization from hot methanol yielded, in 3 crops, a total of 12.1 g of anhydrous sedoheptulosan having m.p. and mixed m.p. of 154–155°. The identifications of the *myo*-inositol and sedoheptulosan were further confirmed by paper chromatography.

The mother liquor from the crystallization of these two compounds was evaporated to a dry syrup that weighed 13.8 g. A solution of a portion of this syrup (6.7 g, equivalent to 37.5 kg of *S. spectabile*) in water was concentrated to a small volume, and placed on the top of a column (93 × 4.5 cm) of Dowex 50W-X8 (Ba²⁺) ion-exchange resin. The column was eluted slowly with water, with use of an automatic fraction-collector. Although the fractionation failed to give any clear-cut separation into the nine or ten components that were evident on paper chromatograms, there was no more than a faint trace of a spot visible in the area where the octitol should appear, even when the chromatograms sprayed with ammoniacal silver nitrate were kept in the dark for two weeks.

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