

Extracellular Polysaccharides of Phytopathogenic Fungi*

DENIS DUBOURDIEU

*Institut d'Oenologie, Université de Bordeaux II
351, Cours de la Libération, 33405 Talence, France
Tel. 56 80 77 91 Telex 550415F*

Abstract

Worldwide consumption of water soluble gums is gradually increasing. The first use of these gums is based on their ability to modify the rheological properties of water solutions. Traditional industrial gums (pectin, arabic gum. . .) are obtained from higher plants or seaweeds. They are difficult to purify, suffer from a lack of reproducibility in their rheological properties, and their production cost is very high. This has stimulated research for microbial polysaccharides that can be produced under controlled conditions. Several phytopathogenic microorganisms are known to be good producers of exocellular polysaccharides. Some of them are of commercial importance. But, one can expect that new polysaccharides will be found in microbial sources. This paper reports the main molecular structures and some industrial applications of polysaccharides secreted by phytopathogenic fungi.

Keywords: water soluble gums, exocellular polysaccharides, glucans

1. α -Glucan

Amylose: (1 \rightarrow 4)- α -D-glucan

Many capsulated yeasts of the genus *Cryptococcus* produce starchlike polysaccharides in liquid medium at pH 5 or below.

Production of "starch" by some species of *Rhodotorula* has also been reported (Gorin and Spencer, 1968).

*Reviewed

Pullulan: (1 → 4 : 1 → 6)-α-D-glucan

The yeast-like fungus *Pullularia pullulans* produces 2 kinds of exocellular glucans (Bouveng et al., 1963): a (1 → 3 : 1 → 6)-β-D-glucan of sclerotan type (see below) and a (1 → 4 : 1 → 6)-α-D-glucan named pullulan.

Pullulan is a linear polysaccharide made up of maltotriose repeating units that are polymerized through α-D-(1 → 6) linkages. Enzymolysis of pullulan by an endo-α-(1 → 6)-glucanase gives mainly maltotriose and minor fragments of maltotetrose (Fig. 1).

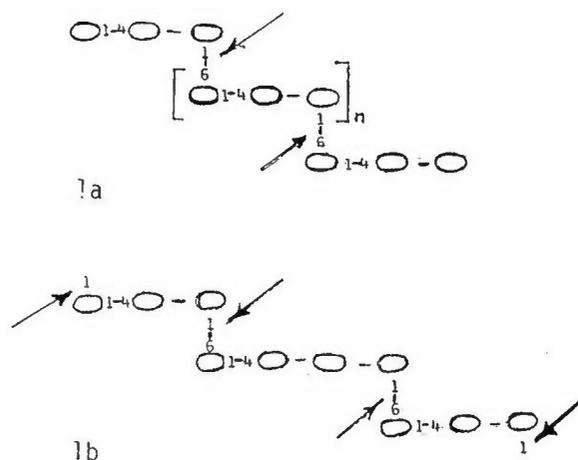


Figure 1. Molecular structure of pullulan (Marshall, 1974).

1 a = general structure

1 b = position of maltotetrose residue in the chain. Hydrolysis by pullulanase.

Large scale productions of pullulan have been reported. The rate of conversion of sucrose in pullulan is very high (70%). Several applications of pullulan have been proposed. Pullulan films are water soluble and impervious to oxygen. They are suitable for coating and packaging foods and for pharmaceuticals.

Other applications have been patented for fiber production (Kato and Shiosaka, 1975). Because of its rheological properties, pullulan can be used as a texture agent in the food industry. This polysaccharide is undigestible but can be degraded by microbial organisms.

2. β-glucans

The pachyman, β-(1 → 3)-glucan

The most common example of β-(1 → 3)-glucan, pachyman is found in sclerotia of a wood degrading fungus, *Poria cocos* (Clark and Stone, 1963).

Non soluble in water but in alkalis, its structure and properties are similar to three other plant polysaccharides: paramylon from some algae (Euglenophytes), laminarine from algae of the genus *Laminaria*, and callose, the gum of higher plants. This last one closes sheath when the inner bark stops to work or is damaged. Laminarin is used in enzymology for β-(1 → 3)-glucanase assay.

β-(1 → 6)-glucan

Lutean from *Penicillium luteum* and islandican from *P. islandicum* have been the first fungal β-(1 → 6)-glucan isolated. Exocellular polysaccharides similar to lutean have been reported in various strains of *Penicillium* (Gorin and Spencer, 1968). These water soluble glucans are partially esterified by malonic acid. The differences between them are the quantities of glucose and malonic acid released by endo-β-(1 → 6)-glucanases. Large scale production of islandican has been patented. This polymer may have uses as an additive for food and cosmetics (Nakamura et al., 1963).

β-(1 → 6)-glucans

Scleroglucans

They are exocellular or reserve glucans. Their molecules are made of a β-(1 → 3) linked glucan backbone with β-(1 → 6) linked side chains of single glucose unit. They have been isolated from sclerotia or culture filtrate from some species of genera *Sclerotium*, *Carticium*, *Sclerotinia*, *Stromatinia*.

One of the first glucans of this type has been isolated from culture filtrates of *Sclerotium rolfii* by Johnson et al., 1963 (Fig. 2). This sclerotan is industrially produced, initially by Pillsbury Co. (Minneapolis, MN, U.S.A.) under the commercial name polytran, and now by CECA SA (Vélizy-Villacoublay, France) under the name Actigum (Rodgers and Goffette, 1976). Scleroglucan might have many industrial uses including paints, industrial coatings, cosmetics and food industry. The largest potential use would be in enhanced oil recovery (Sanford, 1979). In this application, it would replace xanthan, the bacterial gum from *Xanthomonas* (3000 tons of worldwide consumption in 1980).

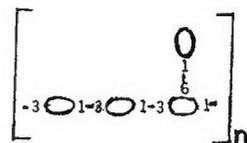


Figure 2. Molecular structure of sclerotan of *Sclerotium rolfsii* (Johnson et al., 1963).

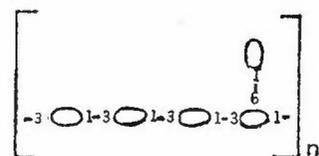


Figure 3. Molecular structure of the (1 → 3 : 1 → 6)-β-D-glucan from *Claviceps purpurea* (Perlin and Taber, 1963).

β-glucans, structurally related to sclerotan are also secreted by other fungi: *Claviceps purpurea* (Perlin and Taber, 1963) (Fig. 3), *Pullularia pullulans* (Bouveng et al., 1963) (Fig. 4).

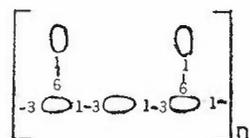


Figure 4. Molecular structure of the exocellular β-glucan from *Pullularia pullulans* (Bouveng et al., 1963).

Botrytis cinerea produces also a β-(1 → 3 : 1 → 6)-glucan similar to sclerotan (Dubourdeiu et al., 1981). This polymer is produced in synthetic media but can be also found in parasited grapes. This glucan is responsible for clarification difficulties in enology. It is degraded by an exo-β-(1 → 3)-glucanase submitted to catabolic repression by the glucose of the medium. A commercial β-(1 → 3)-glucanase (glucanex, NOVO Industry, Denmark) from *Trichoderma harzianum*, which is able to hydrolyse the glucan of *Botrytis* in the wine is now available (Dubourdeiu et al., 1985).

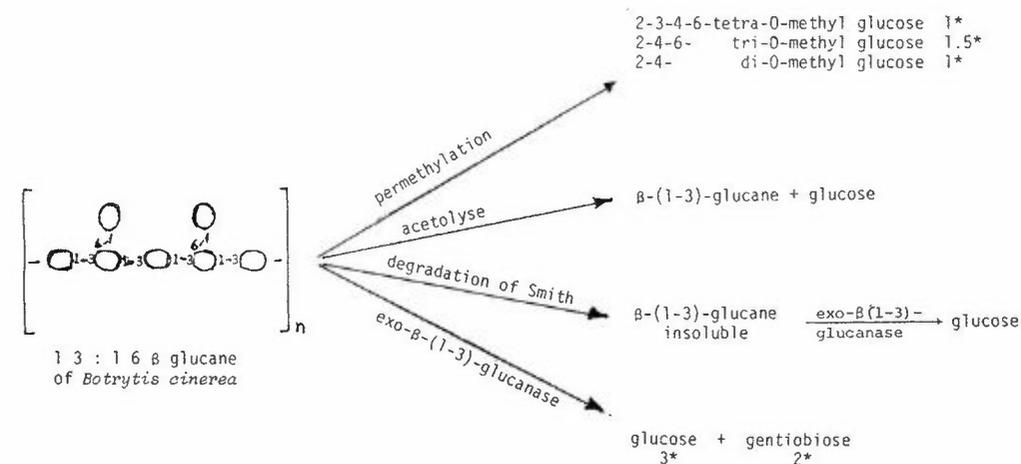


Figure 5. Molecular structure of the β-D-glucan from *Botrytis cinerea* (Dubourdeiu et al., 1981).

REFERENCES

- Bouveng, H.O., Kiessling, H., Lindberg, B. and McKay, J. 1963. Polysaccharides elaborated by *Pullularia pullulans*. *Acta Chem. Scand.* **17**: 1351.
- Dubourdeiu, D., Ribereau-Gayon, P., and Fournet, B. 1981. Structure of the extracellular β-D-glucan from *Botrytis cinerea*.
- Dubourdeiu, D., Desplanques, C., Villetaz, J.C., and Ribereau-Gayon, P. 1985. Investigations of an industrial β-D-glucanase from *Trichoderma harzianum*. *Carbohydr. Res.* **144**: 277-281.
- Gorin, P.A.J. and Spencer, J.F.T. 1968. Structural chemistry of fungal polysaccharides. *Adv. in Carbohydr. Chemistry* **23**: 367-417.
- Kato, K. and Shiosaka, M. 1975. *U.S. Patent* 3,912,591.
- Nakamura, N., Oyama, J., and Tanabe, O. 1963. *Japan Patent* 12 750; *Chem. Abstracts* **59**: 9281.
- Rodgers, N.E. and Goffette, H.R. 1976. Polytran: trade mark of Scleroglucan. *C.E.C.A. S.A. Vellizy Villacoublay*.
- Sanford, P.A. 1979. Exocellular microbial polysaccharides. In: *Adv. in Carbohydr. Chem. and Biochem.* **36**: 265-313.