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Synthesis and characterization of a new methacrylate monomer derived from the cashew nut shell liquid (CNSL) and its effect on dentinal tubular occlusion

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ABSTRACT

Objective. The aim of this study was to synthesize, to characterize and to evaluate the effects on tubular occlusion of new monomer derived from cashew nut shell liquid (CNSL), also studying the effects of acid challenge (AC) on dentin surfaces treated with desensitizers.
Methods. The intermediary cardanol-epoxy (CNE) was synthesized through epoxidation of CNSL, followed by synthesis of cardanol-methacrylate-epoxy (CNME) through methacryloyl chloride esterification. Products were purified through chromatography column and characterized by Fourier transform infrared spectrometry and nuclear magnetic resonance. Resinous dentin desensitizers were formulated containing either unsaturated cardanol (CNU), CNE or CNME. Dentin disks were divided into seven groups: SL — Smear-layer, EDTA — EDTA-treated only, GLUMA — Gluma Desensitizer, OCB — One Coat Bond, CNU — CNU desensitizer, CNE — CNE desensitizer and CNME — CNME desensitizer. Dentinal fluid rate (DFF) was obtained using a Flodec equipment and tubular occlusion employing a scanning electron microscope (SEM), before and after AC. Data of DFF were submitted to two-way ANOVA and Tukey's test ($p < 0.05$).
Results. GLUMA showed the lower reduction in DFF when compared to the other products, which were statistically similar. Even after AC, CNME presented the most homogenous and occluded surface, while CNE and CNU were partially removed, GLUMA was completely removed and OCB keep an occluded, but irregular surface.
Significance. CNME showed a great reduction of DFF and a homogenous occluded surface, suggesting that it may be a suitable and acid-resistant treatment option for dentine hypersensitivity.

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1. Introduction

Hypersensitive dentin (DH) is a common oral health issue in the adult population, associated with exposed cervical dentin and characterized by short and sharp pain in response to several external stimuli [1,2]. This significant increase in the dentin sensitivity is explained by the most widely accepted "hydrodynamic theory" proposed by Brännström et al. [3]. Such explanation advocates that movements of fluid within the dentinal tubules stimulate pulpal mechanoreceptors, which are interpreted as pain. This clinical condition affects directly the quality of life, thereby motivating the investigations of mechanisms leading to DH and the development of a wide range of treatment methods to prevent, reduce or eliminate this condition [4].

Several desensitizing agents have been assessed for the treatment of DH, relying on two approaches: nerve desensitization or occlusion of patent dentinal tubules [5]. However, in agreement with the hydrodynamic theory [3], most of the currently employed agents are used to occlude the dentinal tubules, once this strategy may suppress dentinal fluid movement regardless the stimuli evoked, thereby decreasing DH. Although many studies have reported the initial efficacy of these agents, most of them have their therapeutic effects readily arrested or diminished over time due to daily tooth brushing or intermittent consuming of acidic beverages [6].

Gluma Desensitizer (Hereaus Kulzer, Hanau, Germany) is one of the desensitizing agents with the longest history of use in dental clinics. Its mechanism of action relies on precipitation of plasma proteins within dentinal tubules thanks to the high capacity of glutaraldehyde in promoting protein crosslinking. Nevertheless, such compound is highly detrimental to the metabolism of odontoblast-like pulp cells (MDPC-23) [7] and possesses high dissolution capacity in acidic solutions [8], what might cause several cytotoxic issues. Recently, several more biocompatible plant-derived products were investigated in order to replace glutaraldehyde as dentin collagen crosslinking agent [9]. In this regard, new monomers could be created from these plant-derived compounds yielding improved desensitizing agents.

Cashew nut shell liquid (CNSL) emerges as an abundant renewable resource of naturally occurring phenols, also highlighting affinity with dentin collagen and potential to form crosslinking [10]. After the industrial thermal treatment, CNSL is mainly composed by cardanol (approximately 70%), a long carbon chain phenol (Fig. 1), which grants this compound high hydrophobicity and many reactive sites for organic synthesis [11]. Besides, it does not depict cytotoxic or mutagenic effects [12]. Advances in the development of long-lasting dentin sealing technologies should achieve acid-resistant desensitizing agents. Therefore, the synthesis of a methacrylate epoxy cardanol monomer could obtain biocompatible, hydrophobic and acid-resistant agent, once the oxirane ring can open in acid environments [13,14] and act as a latent polymerization improving the material over time.

The aim of this manuscript was to synthesize, to characterize and to evaluate the effects on dentin desensitization (tubular occlusion) of new methacrylate monomer derived from the CNSL, also studying the effects of acid challenge on dentin surfaces treated with desensitizers. The study hypotheses under investigation were that (1) there are differences in the dentinal tubule occlusion among the desensitizing agents, and (2) the new monomer can promote acid resistance.

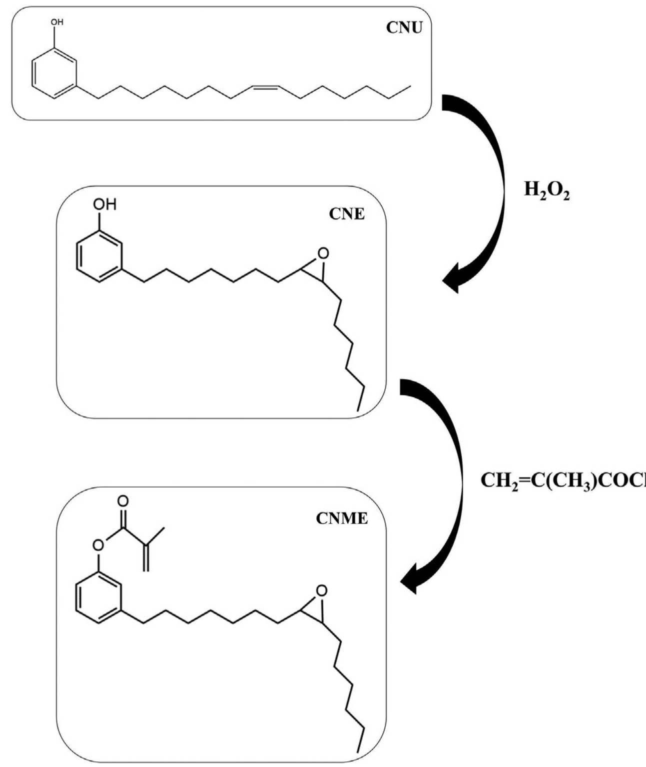

Fig. 1 – Synthetic route: unsaturated cardanol (CNU) was epoxidized with hydrogen peroxide, using formic acid as a catalyst, in order to incorporate an oxirane ring where the unsaturation was located and form cardanol-epoxy (CNE). CNE was esterified with methacryloyl chloride, in the presence of triethylamine as a catalyst, to incorporate one methacrylate functionality where the hydroxyl was located and to obtain the final monomer cardanol-methacrylate-epoxy (CNME).

2. Materials and methods

2.1. Reagents

CNSL (technical grade) was kindly supplied by Amêndoas do Brasil LTDA (Fortaleza, Brazil). Formic acid, hydrogen peroxide, triethylamine, 3,5-Di-tert-4-butylhydroxytoluene (BHT), methacryloyl chloride, anhydrous sodium sulfate and solvents were purchased from Sigma-Aldrich (St. Louis, USA) and used as received. Silica gel (Merck) was employed in the chromatographic separations.

2.2. Synthesis of cardanol-epoxy (CNE)

Briefly, thecardanol-epoxy (CNE) synthesis was accomplished with epoxidation reaction of unsaturations of the CNSL, using hydrogen peroxide and formic acid with a molar ratio of 1:3:1,

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