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NEW APPROACH TO POLYISOPRENEPOLYOLS POSSESSING GLYCEROL TERMINI BY USING A HIGHLY OXYGENATED C_5-UNIT

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Abstract: Polyisoprenepolyols possessing glycerol termini have been synthesized by using 4-(1,2-epoxy-1-methylethyl)-2-phenyl-1,3-dioxolane as a novel highly oxygenated C_5-unit.

Some polyisoprenepolyols with glycerol termini such as phytantriol have long been used as emulsifiers or detergents for skin- and hair-treatment.[1] Recently, unique polyisoprenepolyols which contain multiple tertiary hydroxy moieties as well as glycerol termini have been isolated from *Gymnopilus spectabilis*.[2]

The glycerol termini can be constructed by epoxidation of corresponding allylic alcohols followed by ring opening of the resulting epoxides.[1] However, this method has a difficulty in application to the substrates having other tertiary hydroxy groups, owing to dehydration in the strongly acidic medium. Here we describe a new approach to polyisoprenepolyols with glycerol termini by using a highly oxygenated C_5-unit **1** (Scheme 1).

The synthesis of the novel C_5-unit **1** is as follows (Scheme 2): 1,2-epoxy-3-methyl-3-butene prepared from prenyl acetate *via* ene-type chlorination in 45-55% yield [3] was converted to a dioxolane **4** in 72% yield by reacting with benzaldehyde in the presence of tetrakis(triphenylphosphine)palladium.[4] Epoxidation of **4** with *m*-chloroperbenzoic acid afforded **1** in 88% yield.[5]

A variety of organometals, *i.e.* Grignard reagents in the presence of dilithium tetrachlorocuprate and alkynylalanes prepared from propargylic alcohols, was reacted with **1** to give coupling products **2a**-**d** in 70-95% yield (Table). Hydrogenolysis of the dioxolane moieties of **2a**-**d** was carried out in the presence of palladium black and *p*-toluenesulfonic acid (5-12 mol% based

Scheme 1.

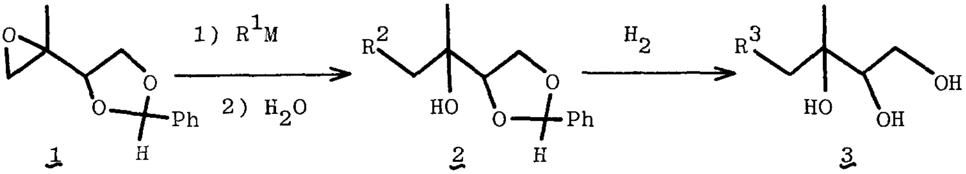
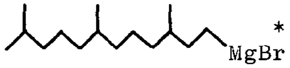
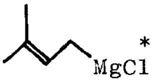
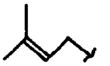
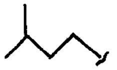
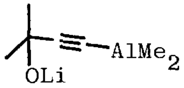
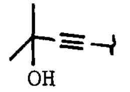
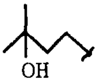
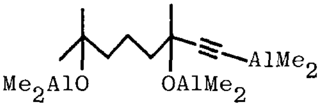
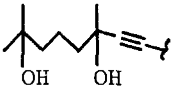
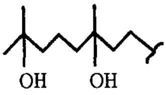


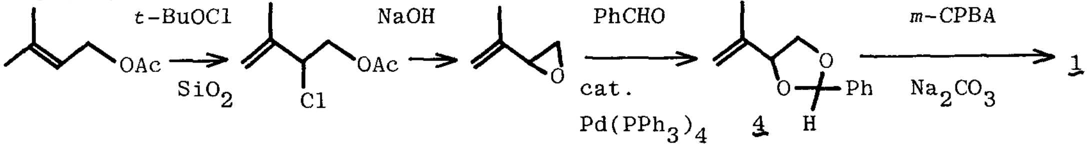
Table.

R^1M	2	$R^2=$	Y. (%)	3	$R^3=$	Y. (%)
 *	2a	R^1	95	3a¶	R^1	78
 *	2b		83	3b		86
	2c		75	3c		89
	2d		70†	3d		72

* Li_2CuCl_4 (4 mol% based on 1) was used as a catalyst.

† Based on the consumed 1.   ¶ Phytantriol.[1]

Scheme 2.



on 3a-d) in ethanol. In the case of 2c and 2d, it was necessary to hydrogenate the acetylenic bonds with palladium on carbon in ethyl acetate prior to the hydrogenolysis. Consequently, polyisoprenepolyols 3a-d were synthesized in 50-74% yield from the C_5-unit 1 (Table).

To our knowledge, this is the first method of synthesizing polyisoprenepolyols possessing both glycerol termini and other tertiary hydroxy moieties.

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References and Notes:

1. *Chem. Abstr.*, 59, 5206f (1963); F. Hoffmann-La Roche & Co., A.-G. (by W. Guex, R. Ruegg, S. F. Schaeren).
2. S. Nozoe, Y. Koike, N. Ito, G. Kusano, *Chem. Lett.*, 1001 (1984).
3. S. Suzuki, Y. Fujita, Y. Kobayashi, F. Sato, *Synth. Commun.*, accepted.
4. T. Fujinami, T. Suzuki, M. Kamiya, S. Fukuzawa, S. Sakai, *Chem. Lett.*, 199 (1985).
5. 1: b.p. 113-118°C / 0.9 torr.
   NMR ($Me_3SiOSiMe_3$ / $CDCl_3$) δ 1.31, 1.34, 1.39 (s, 3H); 2.56-3.00 (m, 2H); 3.81-4.33 (m, 3H); 5.74, 5.83, 5.93 (s, 1H); 7.39 (m, 5H).
   IR (film) ν 1095, 1075, 705 cm^{-1}.
   MS *m/z* (*rel. int.*) 105 (100), 91 (58), 205 (38), 206 (13, M^+).

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