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Carbohydrate Research 302 (1997) 219–221

CARBOHYDRATE RESEARCH

Note

A new glycoside, 1D-2-*O*-α-D-galactopyranosyl-*chiro*-inositol from jojoba beans

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Received 16 January 1997; accepted 21 February 1997

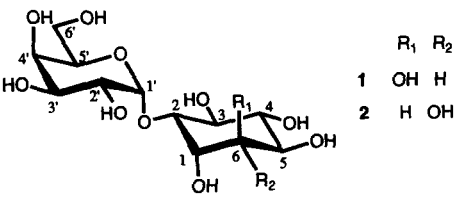
Abstract

A new inositol glycoside, 1D-2-*O*-α-D-galactopyranosyl-*chiro*-inositol has been isolated from jojoba plant, *Simmondsia chinensis*. © 1997 Elsevier Science Ltd.

Keywords: *Simmondsia chinensis*; Jojoba beans; Inositol glycoside; 1D-*chiro*-Inositol; NMR spectrometry

1. Introduction

The jojoba plant, *Simmondsia chinensis*, is a shrub which grows in arid areas. Jojoba oil is extracted from its beans. Carbohydrates found in the residual bean meal (defatted beans including hulls) include simmondsin and its 2′-ferulate, isolated by Elliger et al. [1–4], and 4-β-galactobiose and 4-β-galactotriose by Watanabe and Matsuda [5]. A new inositol glycoside, 1D-2-*O*-α-D-galactopyranosyl-*chiro*-inositol (**1**) has been isolated from defatted jojoba beans, in addition to the known D-pinitol [6] and galactinol (**2**) [7,8]. The isolation and structural elucidation of the new glycoside are presented. The structure was determined by acid hydrolysis and extensive NMR spectroscopic studies.



2. Results and discussion

Jojoba beans (1000 g) were heated with boiling water, and the beans were peeled, crushed, defatted with a 2:1 mixture of benzene–ethanol at 50 °C, and disintegrated into fine pieces. The resulting powder was extracted with 80% ethanol in a boiling-water

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PII S0008-6215(97)00092-X

bath to afford a syrup (34.5 g). The syrup was chromatographed on a column of activated charcoal–diatomaceous earth, and a mixture (3.81 g) of several carbohydrates was obtained from the 5% ethanol eluate. The mixture was further purified by preparative PC to yield three pure compounds having R_f 0.56, 0.19, and 0.11. The new glycoside (**1**, 170 mg) having R_f 0.19 was isolated as a colorless solid: mp 165–170 °C (decomp); $[\alpha]_D^{24}$ +130° (*c* 0.5, H_2O). The second compound (**2**, 155 mg) of R_f 0.11 was identical with galactinol (1L-1-*O*-α-D-galactopyranosyl-*myo*-inositol [1]) isolated from sugar-beet juice [7,8]. The third compound (346 mg) of R_f 0.56 was identical with D-pinitol (1D-3-*O*-methyl-*chiro*-inositol) widely distributed in plants [6].

Acid hydrolysis of **1** with 2 M trifluoroacetic acid, followed by preparative PC, gave two components which were identical with authentic samples of D-galactopyranose and 1D-*chiro*-inositol. The structure of **1** ($C_{12}H_{22}O_{11}$) was determined to be 1D-2-*O*-α-D-galactopyranosyl-*chiro*-inositol by NMR measurements (^1H–^1H COSY, ^{13}C–^1H COSY, and differential NOE). The coupling constant (*J* 3.9 Hz) of 1′-H (δ 5.14 d) showed an α-glycosidic linkage of the D-galactopyranoside. The chair conformation ($^2C_5$) of the inositol moiety was elucidated from the 1,3-diaxial relation of 2-H (δ 3.83) and 4-H (δ 3.64), and the *cis* relation of 2-H and 1-H (δ 4.23) by NOE. In addition, a NOE between 1′-H and 2-H suggested that 1-H and 2-H are on the same side of 1′-H. This compound **1** is a new glycoside, different from such known D-*chiro*-inositol glycosides as 1D-2-*O*-(α-D-galactopyranosyl)-4-*O*-methyl-*chiro*-inositol (galactopinitol) [9,10] isolated from seeds of subterranean clover, and an antibiotic kasugamycin [11] (the 3-*O*-glycoside) produced by a streptomycetes.

[1] The nomenclature conforms with the IUPAC-IUB 1973 Recommendations for Cyclitols. This compound was reported by Kabat et al. [8] as D-1-*O*-α-D-galactopyranosyl-myoinositol in 1953.

3. Experimental

General methods.—Melting points were obtained with an Electrothermal IA9100 digital melting point apparatus and are not corrected. Optical rotations were taken on a Perkin–Elmer 241 polarimeter. IR spectra were recorded with a Horiba FT210 spectrophotometer. Mass spectra were determined with a Jeol JMS-SX102 mass spectrometer (FAB mode). ^1H NMR spectra were measured with a Jeol JNM-EX400 or JNM-A500 spectrometer using sodium 4,4-dimethyl-4-silapentanoate (δ 0) as the internal standard, and ^{13}C NMR spectra were recorded in D_2O at 50 °C with 1,4-dioxane (δ 67.4) as standard. Ascending PC was carried out using Toyo No. 50 filter paper (Toyo Roshi Kaisha, Ltd., Japan), with a 6:4:3 mixture of 1-butanol–pyridine–water as the developing solvent, and the compounds were detected with $AgNO_3$ reagent.

Isolation.—Jojoba beans (50.0 g) were heated with boiling water (200 mL) for 1 h. After being peeled and crushed, the beans were defatted with a 2:1 mixture of benzene–EtOH (240 mL, twice) at 50 °C for 3 h, and disintegrated into fine pieces (16.4 g). Such 20 runs were made to yield 328 g of the defatted powder. The powder was extracted with 80% EtOH (4 L) in a boiling-water bath for 1.5 h to obtain 34.5 g of a syrup. The syrup (34 g) was dissolved in

Table 1
^1H and ^{13}C NMR data for **1** and **2**

Position	**1**			**2**		
	^{13}C (δ)	^1H (δ)	*J* (Hz)	^{13}C (δ)	^1H (δ)	*J* (Hz)
1	68.9	4.23 dd	2.9, 4.2	69.3	4.28 dd	2.4, 2.9
2	76.9	3.83 dd	2.9, 9.5	76.9	3.62 dd	2.4, 9.8
3	72.4	3.72 dd	9.5, 9.5	72.2	3.76 dd	9.3. 9.8
4	73.8	3.64 dd	9.5, 9.5	75.3	3.33 dd	9.3, 9.3
5	71.5	3.79 dd	3.4, 9.5	73.4	3.67 dd	9.3, 9.8
6	72.2	4.07 dd	3.4, 4.2	72.0	3.52 dd	2.9, 9.8
1′	96.9	5.14 d	3.9	96.6	5.13 d	3.9
2′	69.4	3.87 dd	3.9, 10.3	69.3	3.86 dd	3.9, 10.3
3′	70.5	3.95 dd	3.4, 10.3	70.5	3.94 dd	3.4, 10.3
4′	70.3	4.03 dd	1.0, 3.4	70.3	4.02 dd	< 1.0, 3.4
5′	72.0	4.21 dt	1.0, 5.9	72.0	4.18 dd	< 1.0, 6.1
6′	62.0	3.74 d	5.9	62.1	3.73 d	6.1

water (340 mL) and chromatographed on a column of 240 g each of activated charcoal (Kanto Chemical Co., Japan) and diatomaceous earth (Celite 545, Celite Corp., USA) by stepwise elution with water and aq EtOH. After washing the column with water (8 L), a mixture (3.81 g) of several carbohydrates was obtained from the 5% EtOH eluate (3 L). The mixture was further purified by preparative PC which was developed with 6:4:3 1-butanol–pyridine–water to yield three pure compounds having R_f 0.56, 0.19, and 0.11. The pure new glycoside (**1**, 170 mg) having R_f 0.19 was obtained as a colorless solid: mp 165–170 °C (decomp); $[\alpha]_D^{24}$ +130° (*c* 0.5, H_2O); IR (KBr): ν_{max} 3384, 2929, 1631, 1597, 1414, 1228, 1146, 1072, 1024, 806, and 764 cm^{-1}; FABMS (pos): *m/z* 365 $[M + Na]^+$, 343 $[M + H]^+$; FABMS (neg): *m/z* 341 $[M - H]^-$. The ^1H and ^{13}C NMR chemical shifts are shown in Table 1. The second compound (**2**, 155 mg) of R_f 0.11 was identical with galactinol (1L-1-*O*-α-D-galactopyranosyl-*myo*-inositol) [7,8] in all respects, including optical rotation: $[\alpha]_D^{21}$ +131° (*c* 1.0, H_2O), lit. +135.6° [7]. The ^1H and ^{13}C NMR chemical shifts of **2** were assigned as shown in Table 1. The third compound (346 mg) of R_f 0.56 was identical with D-pinitol (1D-3-*O*-methyl-*chiro*-inositol) in all respects including optical rotation: $[\alpha]_D^{23}$ +62° (*c* 0.5, H_2O), lit. +66.8° [6].

Acid hydrolysis of **1**.—Hydrolysis of **1** (40 mg) with 2 M CF_3CO_2H at 100 °C for 4 h, followed by preparative PC gave two dextrorotatory components (6.2 and 12 mg) which were identical with authentic samples of D-galactopyranose and 1D-*chiro*-inositol, respectively, in all respects, including optical rotation values.

Acknowledgements

We thank Ms. Yumiko Ono and Harumi Sato for their assistance in the experimental work. We are indebted to Drs. Masanori Yamaura and Kazuyuki Umemura for their helpful suggestions. Thanks are also due to Dr. Hiroshi Naganawa for the measurements of MS and NMR spectra.

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