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SYNTHESIS OF A MONOESTER OF SUCROSE WITH trans-O-METHYLMARMESINIC ACID

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The water-soluble 6-O-monoester of sucrose with trans-O-methylmarmesinic acid has been synthesized by the transesterification of methyl trans-O-methylmarmezinate with sucrose. The structure of the compound obtained has been confirmed by UR, UV, PMR, and ^{13}C NMR spectroscopies.

Cinnamic acids play an important role in the vital activity of plants and are widespread natural compounds. In plants they are found both in the free state and in the form of esters with carbohydrates or as glycosides [1]. Many of them are biologically active substances. At the present time, the use of natural esters of cinnamic acid with carbohydrates is limited by their poor availability as a consequence of the difficulty of isolating them from plants and the complexity of their synthesis (necessity for using protective groups – acetyl, isopropylidene, etc.), and the formation of by-products when acid chlorides and anhydrides are used [2].

With the aim of developing a simpler and more accessible method of obtaining water-soluble analogues of cinnamic acids, we have studied the possibility of obtaining monoesters of trans-cinnamic acids with sucrose. This expedient, based on the opening of the lactone ring of a furocoumarin, the isomerization of the cis-cinnamic acid so formed to the trans-isomer and the subsequent esterification of a carbohydrate (in the present case, sucrose) with it, has not been described in the literature. As the starting material we used the dihydrofurocoumarin marmesin (I), obtained by the acid hydrolysis of the glycoside marmesinin [3].

It was found that the opening of the lactone ring and cis-trans isomerization takes place without the formation of by-products [4]. In the UV spectrum of product (II) the absorption band in the 335 nm region had disappeared and the band characteristic for trans-cinnamic acids in the 280 nm region was present. The PMR spectrum of compound (II) showed two doublets in the regions of 6.85 and 8.65 ppm with ^3J = 16 Hz due to trans-olefinic protons. We then subjected the trans-marmesinic acid (II) to methylation with diazomethane [5]. This led to the methylation of both the carboxylic and the phenolic hydroxy groups, with the formation of methyl trans-O-methylmarmesinate. Sucrose esters were obtained by a transesterification

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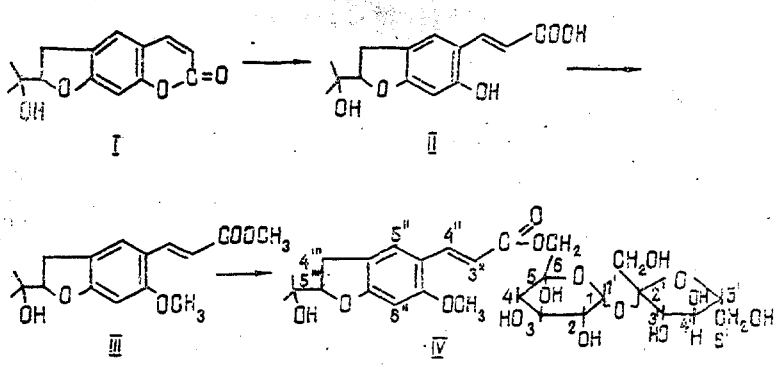
reaction between the methyl ester (III) and sucrose in dimethylformamide in the presence of an alkaline catalyst (K_2CO_3). The monoester acylated in position 6 of the glucose part of the molecule was isolated by column chromatography on silica gel.



The UV spectrum of the monoester was determined by the chromophore of the initial methyl trans-O-methylmarmesinate. The formation of the ester bond in the monoester was confirmed by the presence in the IR spectrum of an absorption band at 1710 cm^{-1}. Bands characteristic for the vibrations of the C=C bonds of an aromatic nucleus were present in the 1500 and 1620 cm^{-1} regions. The IR spectrum also contained bands at 990 and 935 cm^{-1} characteristic for the sucrose moiety of the molecule (the —O—C—O—C—O—C sequence of atoms) and at 3100-3600 cm^{-1} (associated OH).

In the PMR spectrum of the monoester there was a group of signals of the protons of the —CH and CH_2 groups of the sucrose moiety at 3.8-5.2 ppm, the signals of the anomeric proton of glucose at 5.98 ppm, and the signals of the protons of an aromatic ring (6.3-7.3 ppm). The presence of two one-proton doublets at 6.55 and 8.15 ppm (^3J = 16 Hz) was due to trans-olefinic protons.

The position of the acyl residue in the monoester of trans-O-methylmarmesinic acid was determined by ^{13}C NMR spectroscopy. We obtained the specturm of unsubstituted sucrose for comparison. The assignment obtained corresponded to that given in the literature [6].

Below we give the ^{13}C chemical shifts for the carbohydrate moiety of compound (IV) and their differences for the corresponding carbon atoms of the monoester relative to sucrose (δ, ppm; 0 — TMS):

Carbon atom	Sucrose	IV	$\Delta\delta$
1	91.8	92.2	+0.4
2	71.2	71.5	+0.3
3	72.3	72.7	+0.4
4	69.8	70.2	+0.4
5	72.7	70.5	−2.2
6	60.3	63.3	+3.0
1'	62.0	62.5	+0.5
2'	103.7	104.1	+0.4
3'	77.0	77.7	+0.7
4'	74.0	74.5	+0.4
5'	81.3	81.5	+0.2
6'	61.8	62.2	+0.4

Acylation at the primary hydroxy group of the glucose residue was confirmed by the fact that the signal of the carbon atom in the α-position to the ester group (C-6) had shifted downfield by 3 ppm, while that in the β-position (C-5 of the glucose residue) had undergone a diamagnetic shift of 2.2 ppm in comparison with the chemical shifts of the corresponding carbon atoms of unsubstituted sucrose. The chemical shifts of the carbon atoms of the other primary hydroxy groups in the fructose moiety of the sucrose molecule had changed insignificantly ($\Delta\delta \pm 0.5$ ppm).

EXPERIMENTAL

UV spectra were recorded on a Specord UV-VIS spectrophotometer, IR spectra on a UR-20 instrument (KBr tablets), and PMR spectra on a Tesla 487 (80 MHz) instrument with HMDS as internal standard in C_5D_5N. ^{13}C NMR spectra were taken on a Bruker WP-80 instrument with a working frequency of 10.15 MHz. The course of the reactions was monitored by TLC on a Silufol UV-254 plate. The substances were purified and separated by column chromatography on silica gel L (0.04-0.1 mm) (Czechoslovakia).

trans-Marmesinic Acid (II). A mixture of 10.0 g (0.041 mole) of marmesin, 300 ml of 2 N NaOH, and 5.0 g (0.023 mole) of HgO was heated under reflux for 3 h and was filtered. The filtrate was acidified with 10% HCl and was left overnight. The yellow-green flocks that had precipitated were filtered off, to give 10.28 g (95.8%) of product (II). After recrystallization from 70% methanol – 6.17 g (60%), mp 203-204°C, R_f 0.68 [chloroform–methanol (4:1)]. Found %: C 63.71; H 6.11; $C_{14}H_{16}O_5$. Calculated %: C 63.63; H 6.06; M^+ 264. IR spectrum (ν_{max}^{KBr}, cm^{-1}): 1670 (CO, ester), 1610, 1500 (Ar), 3580 (–OH tert.), 3260-3460 (–OH). PMR (δ, ppm): 1.20 (3H, s), 1.30 (3H, s); 2.82-3.48 (2H, m; H-4'); 4.69 (1H, t, H-5'); 6.45 (1H, s, H-8); 6.85 (1H, d, H-3, J = 16 Hz); 7.40 (1H, s, H-5); 8.65 (1H, d, H-4, J = 16 Hz); 9.8 (1H, s, phenolic OH).

Methyl trans-O-methylmarmesinate (III). This was obtained by the methylation of compound (II) with an ethereal solution of diazomethane by a known procedure [5]. This gave 11.89 g (81.4%) of (III), mp 52-54°C, R_f 0.86 (chloroform–methanol (4.1)]. Found %: C 65.81; H 6.91; $C_{16}H_{20}O_5$. Calculated %: C 65.75; H 6.85; M^+ 292. UV spectrum ($\lambda_{max}^{ethanol}$, nm): 206, 225, 245, 283 (log ε 3.85; 3.48; 3.39; 3.60). IR spectrum (ν_{max}^{KBr}, cm^{-1}): 1710 (CO, ester), 1610, 1585 (Ar), 3400-3600 (–OH).

6.O-Monoester of Sucrose with trans-O-Methylmarmesinic Acid (IV). With heating to 90-95°C and vigorous stirring, 51.35 g (0.15 mole) of sucrose was dissolved in 100 ml of redistilled dimethylformamide. Then 14.66 g (0.05 mole) of (III) and, as catalyst, 0.75 g (0.0052 mole) of K_2CO_3 (calcined at 300°C) were added. The reaction was carried out at 95-100°C under an inert gas (nitrogen) at a residual pressure of 100-140 mm Hg for 12-15 h. The unchanged sucrose was precipitated with toluene. The solvents were distilled off under vacuum, and the reaction product (IV) was dried at 70°C and a pressure of 5-7 mm Hg. The reaction product was purified by column chromatography with elution by chloroform–methanol (9:1). This gave 10.48 g (34.82%) of substance (IV), soluble in water and alcohol, mp 126-130°C, R_f 0.2 (chloroform–methanol (4:1)]. Found %: C 53.91; H 6.41; $C_{27}H_{38}O_{15}$. Calculated %: C 53.82; H 6.31. UV spectrum ($\lambda_{max}^{ethanol}$, nm): 206, 224, 245, 283 (log ε 3.89; 3.48; 3.34; 3.57). IR spectrum (ν_{max}^{KBr},nm): 1710 (CO, ester), 1610, 1590 (Ar), 3100-3600 (–OH). PMR (δ, ppm): 1.23 (3H, s), 1.34 (3H, s, isopr. gp.), 2.8-3.3 (2H, m, C-4'''); 3.42 (3H, s, $-OCH_3$); 3.8-5.2 (1H-5''' and 7H of sucrose); 5.98 (2H, br. s, anom. H and tert. OH); 6.3 (1H, s, C-8''); 6.65 (1H, d, J = 16 Hz, C-3''); 7.3 (1H, s, C-5''); 8.15 (1H, d, J = 16 Hz, C-4'').

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