Direct conversion of wheat bran hemicelluloses into *n*-decyl-pentosides

Supplementary Data

SinisaMarinkovic, Boris Estrine*[1]

1. ARD (Agro Industrie Recherches Développements), route de Bazancourt, 51110 Pomacle, France.

* Corresponding author. Address: ARD (Agro Industrie Recherches Développements), route de Bazancourt, 51110 Pomacle, France. Tel./fax: +33 326 05 42 80/ +33 326 05 42 89.

E-mail address: b.estrine@a-r-d.fr@a-r-d.fr (B. Estrine).

General information:

Materials and chemicals

n-decanol, H_2SO_4 (96%) and NaOH (50% solution) of analytical grade were used as received (Acros) without further purification. Wheat Straw was used after being chopped with a mixer in order to obtain fibrils of 1-2 mm of length.

NMR, FT-IR and MS/HRMS

NMR spectra were recoded with a Bruker AC 250 (250 MHz for ^{1}H and 62 MHz for ^{13}C). Chemical shifts are given in ppm relative to the residual solvent signal.

IR spectra were recorded on a Nicolet AVATAR 320 FT-IR.

MS and HRMS were obtained on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manshester, UK) operated in positive mode (EV = 30V, 80°C, flow of injection 5ml/min).

All decyl glycosides are known products synthesised as previously described[1].

[1] C. Landreat, Ph.D. Thesis, University of Reims (FR), **1996**. For L-arabinoside standards see also: a) T. McEwan, A. G. McInnes, D. G. Smith, *Carbohydr. Res*. **1982**, *104*, 161; b) R. G. S. Ritchie, N. Cyr, B. Korsch, H. J. Koch, A. S. Perlin, *Can. J. Chem*., **1975**, *53*, 1424; c) R. López A. Fernández-Mayoralas, *J. Org. Chem*. **1994**, *59*, 737. For D-xylosides standards see: a) A. K. Pathak, V. Pathak, J. A. Maddry, W. J. Suling, S. S. Gurcha, G. S. Besra, R. C. Reynolds, *Bioorg. Med. Chem.* **2001**, *9*, 3145; c) S. Matsumura, Y. Kinta, K. Sakiyama, K. Toshima, *Biotech. Letters*, 1996, **18**, 1335.

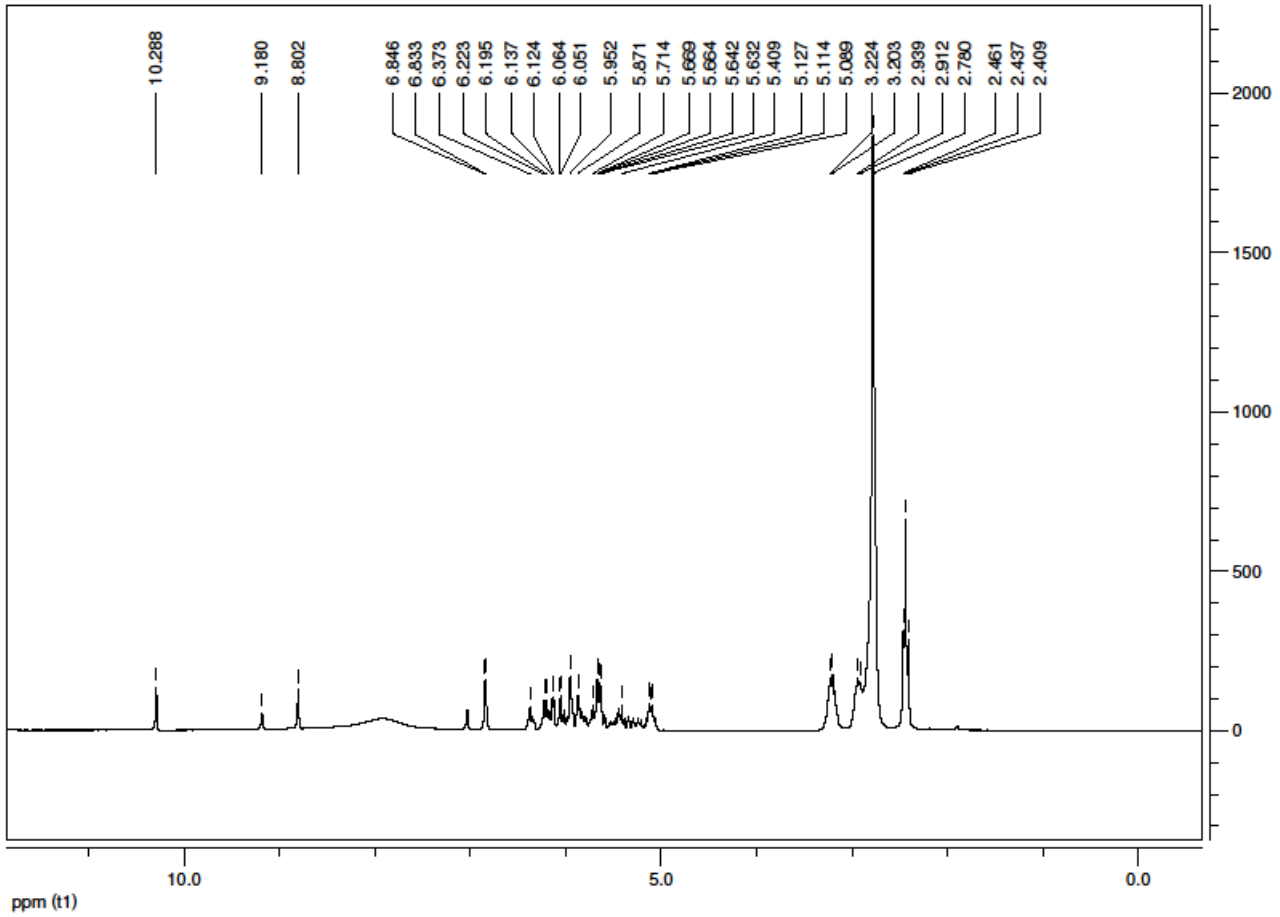
***n*-decyl arabinosides:**

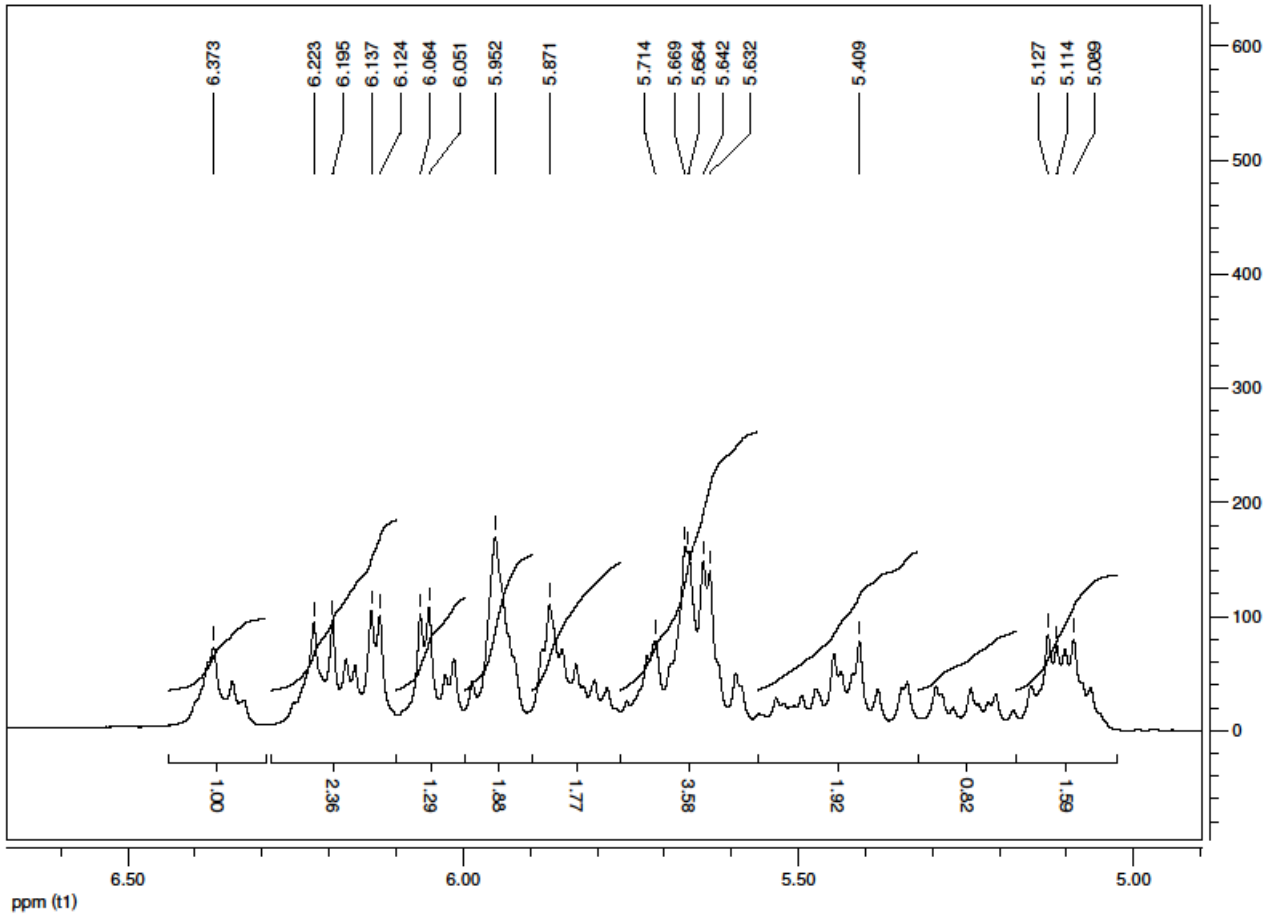
IR : ν_{max} (film)/cm^{-1} : 3378 (F, O-H), 2919, 2852 (F, C-H), 1469 (f, CH_2), 1377 (f, CH_3), 1245 (f, C-O), 1144, 1114 (f, C-OH), 1044 (F, C-OH)

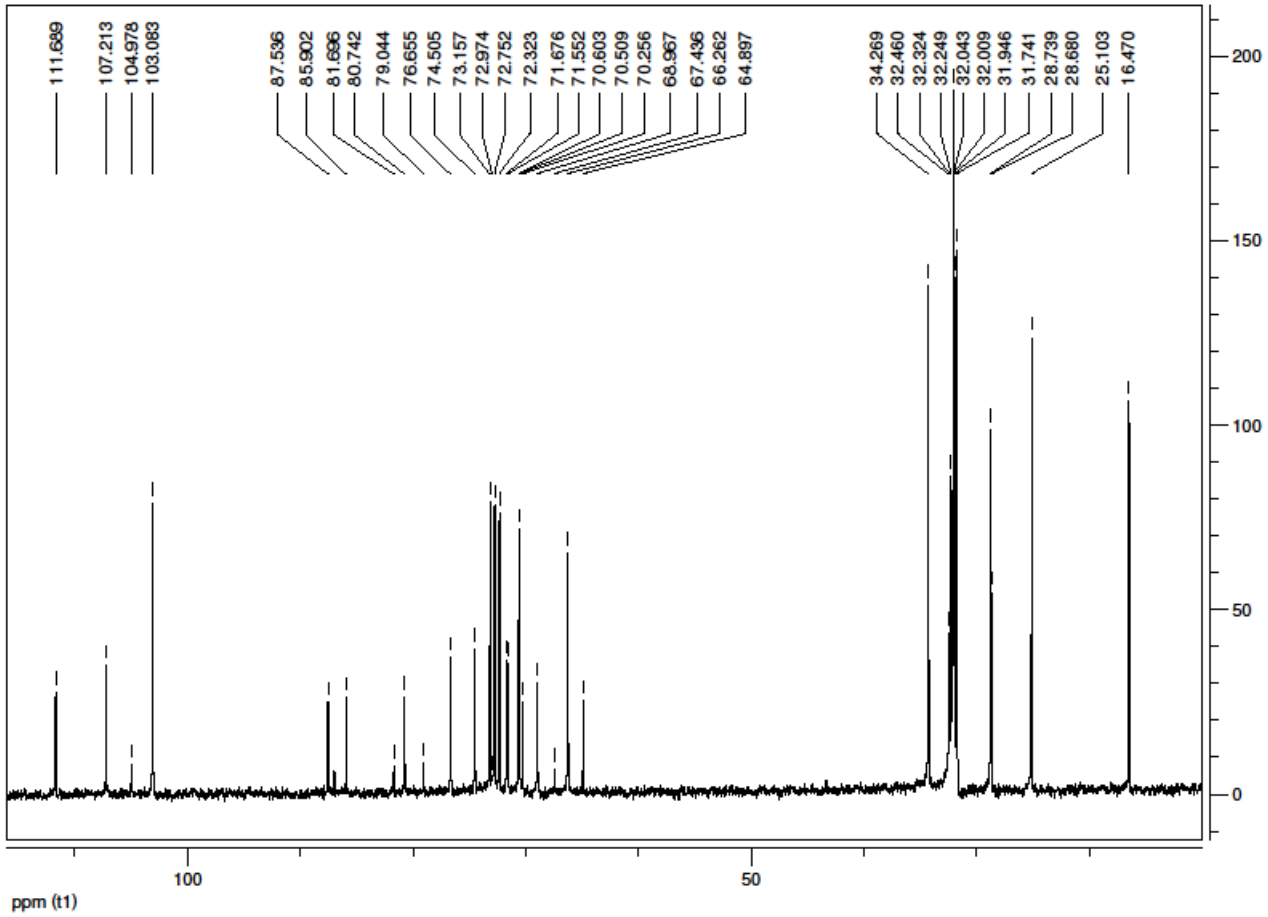
m/z calculated for [$C_{15}H_{30}O_5$ + Na^+], 313,1991, found 313,1980

Elemental analysis ($C_{15}H_{30}O_5$) : Calculated C = 62,04 % ; H = 10,41 %

Found C = 60,02 % ; H = 10,55 %


10.288
9.180
8.802
6.846
6.833
6.373
6.223
6.195
6.137
6.124
6.064
6.051
5.952
5.871
5.714
5.669
5.664
5.642
5.632
5.409
5.127
5.114
5.089
3.224
3.203
2.939
2.912
2.780
2.461
2.437
2.409
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)





m/z calculated for trimethylsilylated standard [$C_{24}H_{58}NO_5Si_3$ +], 524.36, found 524

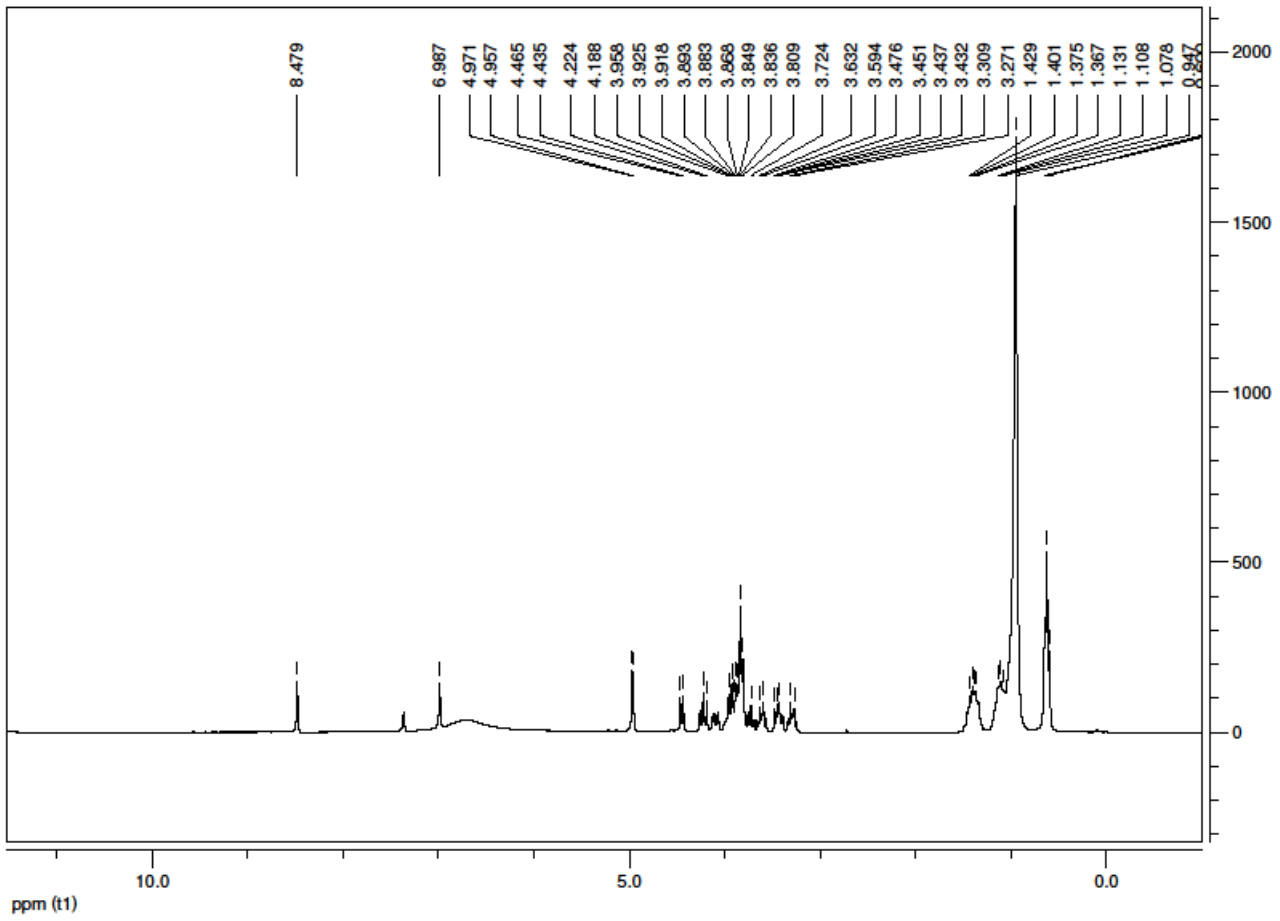
_n_-decyl xylosides

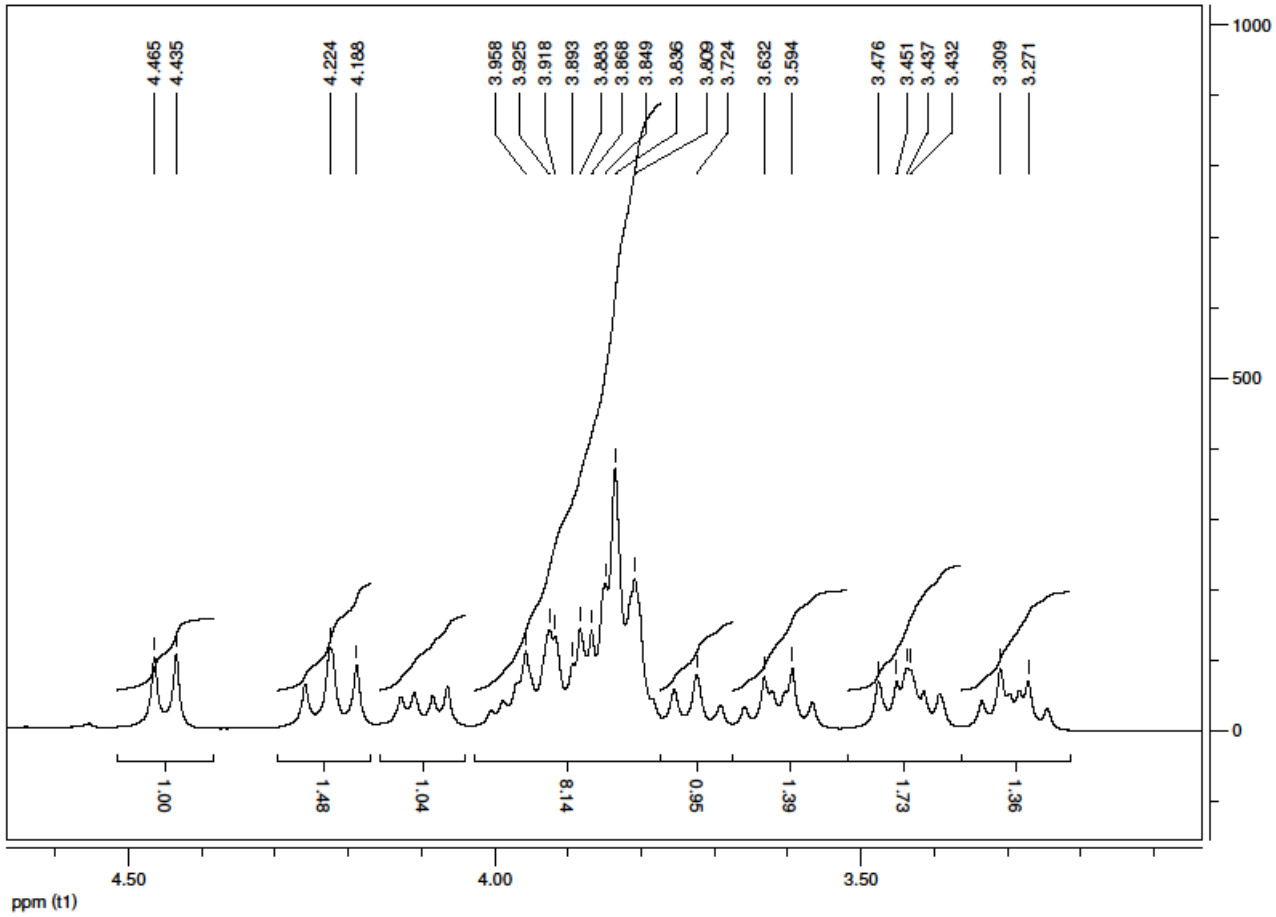
IR : ν_{max} (film)/cm^{-1} : 3378 (F, O-H), 2919, 2852 (F, C-H), 1469 (f, CH_2), 1377 (f, CH_3), 1245 (f, C-O), 1144, 1114 (f, C-OH), 1044 (F, C-OH)

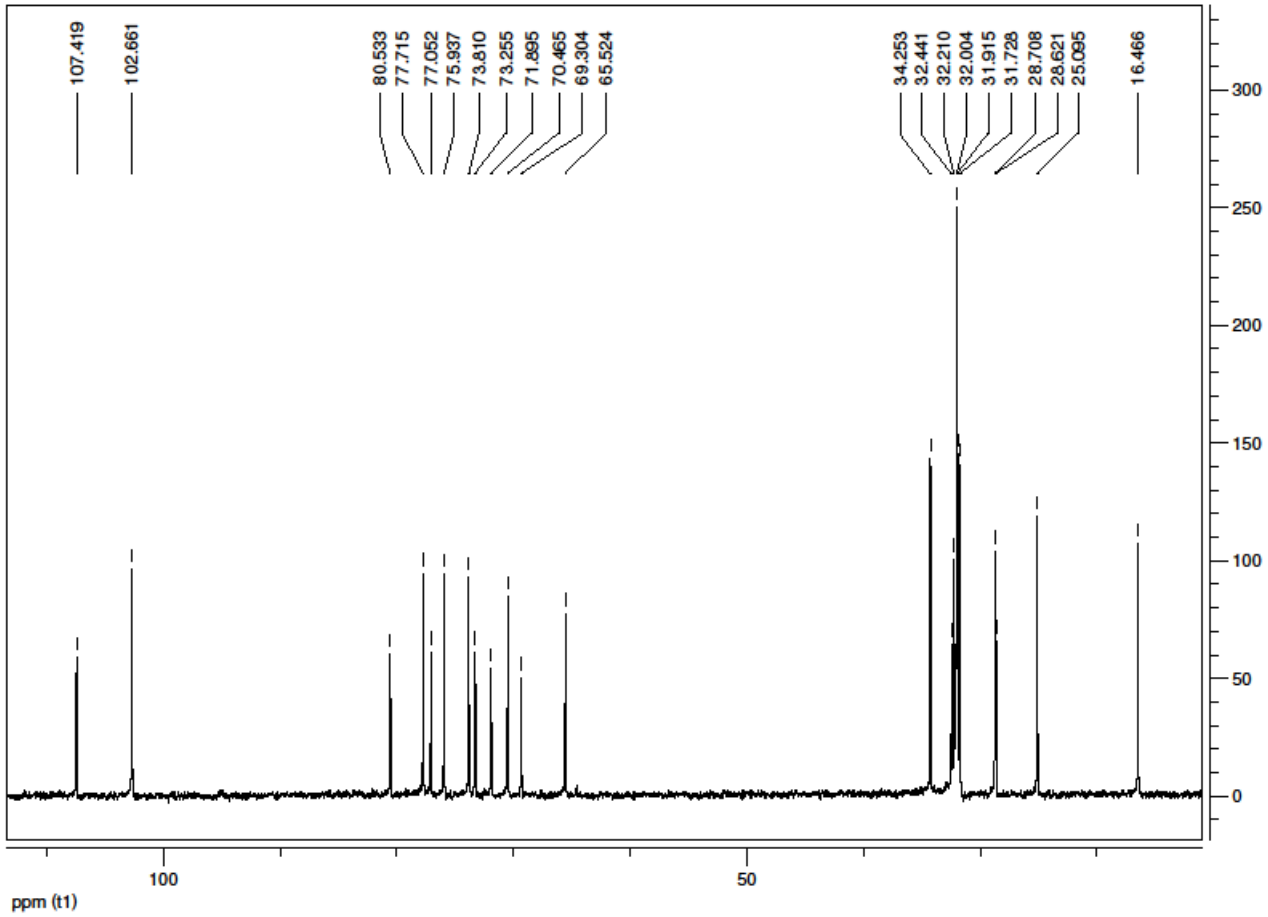
m/z calculated for [$C_{15}H_{30}O_5$ + Na^+], 313,1991, found 313,1980

Elemental analysis ($C_{15}H_{30}O_5$) : Calculated C = 62,04 % ; H = 10,41 %

Found C = 60,02 % ; H = 10,55 %




4.465
4.435
4.224
4.188
3.958
3.925
3.918
3.893
3.883
3.868
3.849
3.836
3.809
3.724
3.632
3.594
3.476
3.451
3.437
3.432
3.309
3.271
1000
500
0
1.00
1.48
1.04
8.14
6.96
1.39
1.73
1.36
4.50
4.00
3.50
ppm (t1)

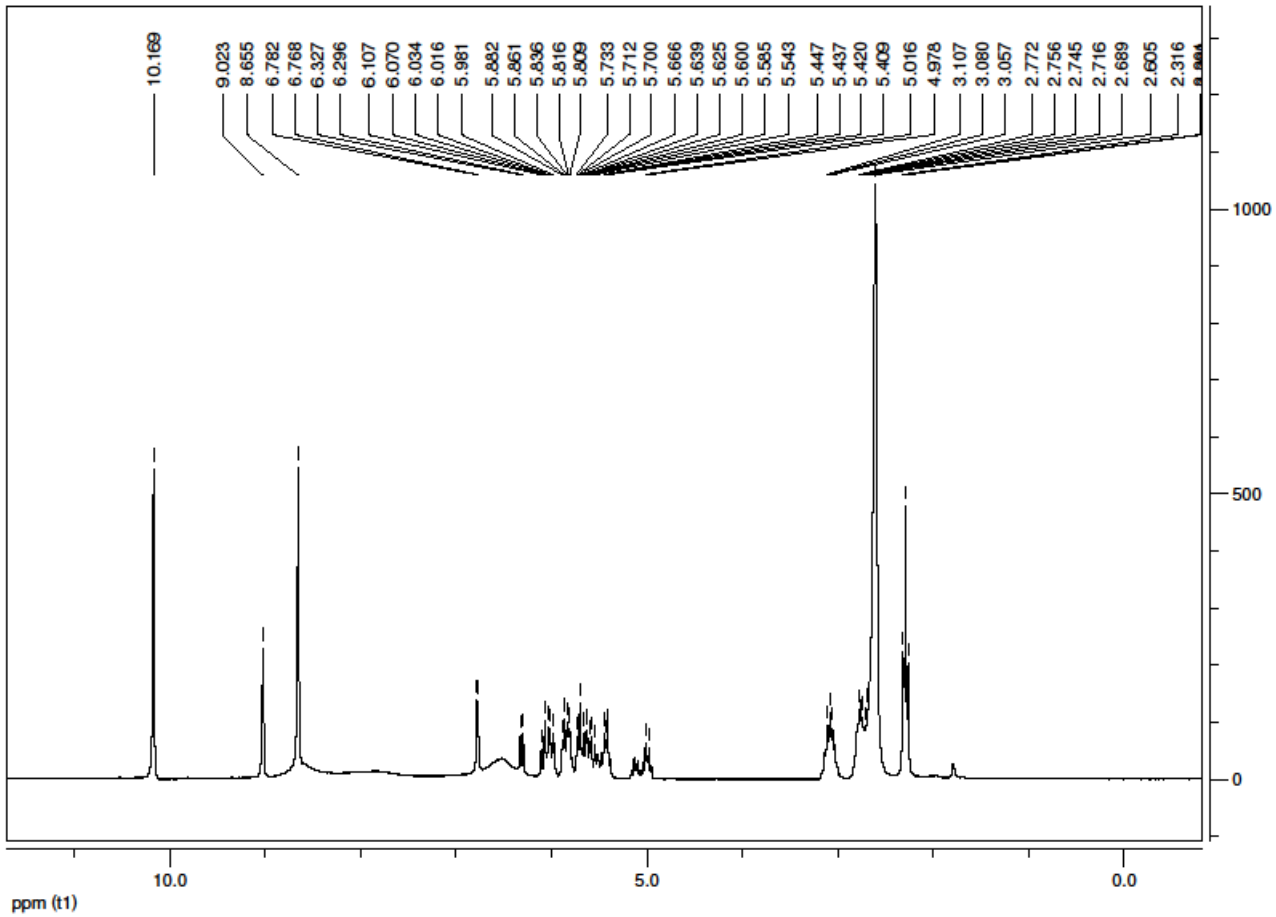


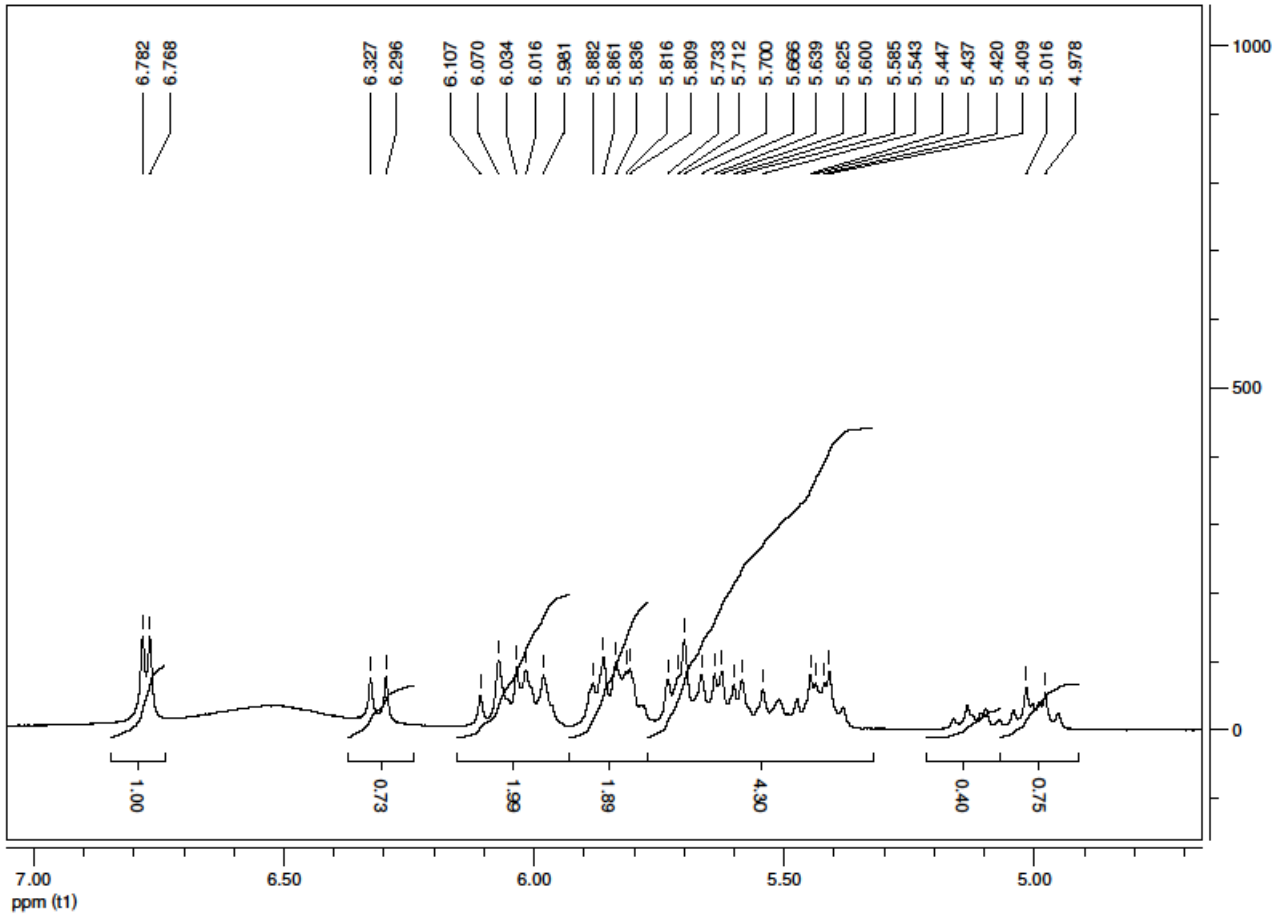
m/z calculated for trimethylsilylated standard [$C_{24}H_{58}NO_5Si_3$ +], 524.36, found 524

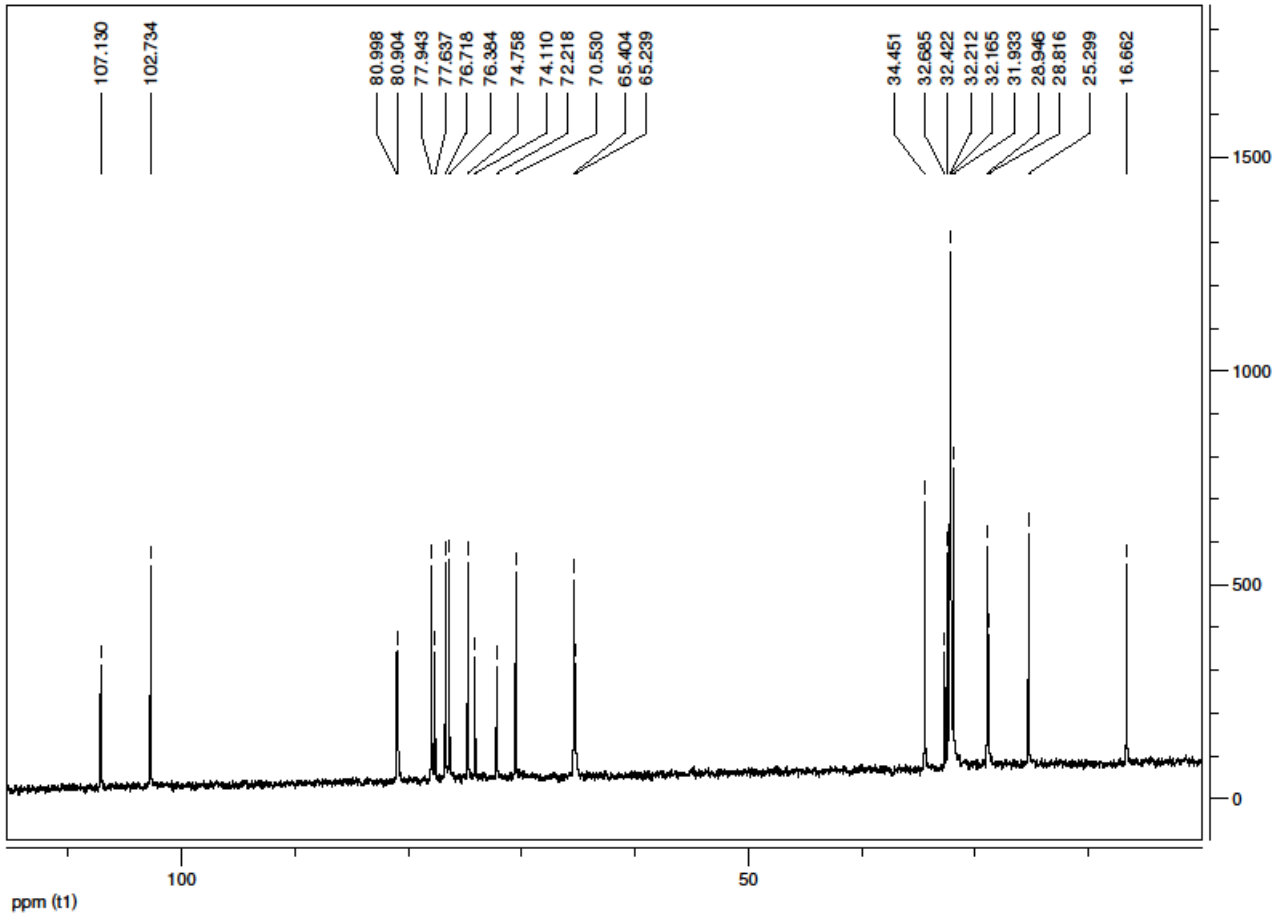
n-decyl glucosides

IR : ν_{max} (film)/cm^{-1} : 3378 (F, O-H), 2919, 2852 (F, C-H), 1469 (f, CH_2), 1377 (f, CH_3), 1245 (f, C-O), 1144, 1114 (f, C-OH), 1044 (F, C-OH)

m/z calculated for [$C_{12}H_{37}O_5$ + Na^+], 341,1784, found 341,1776

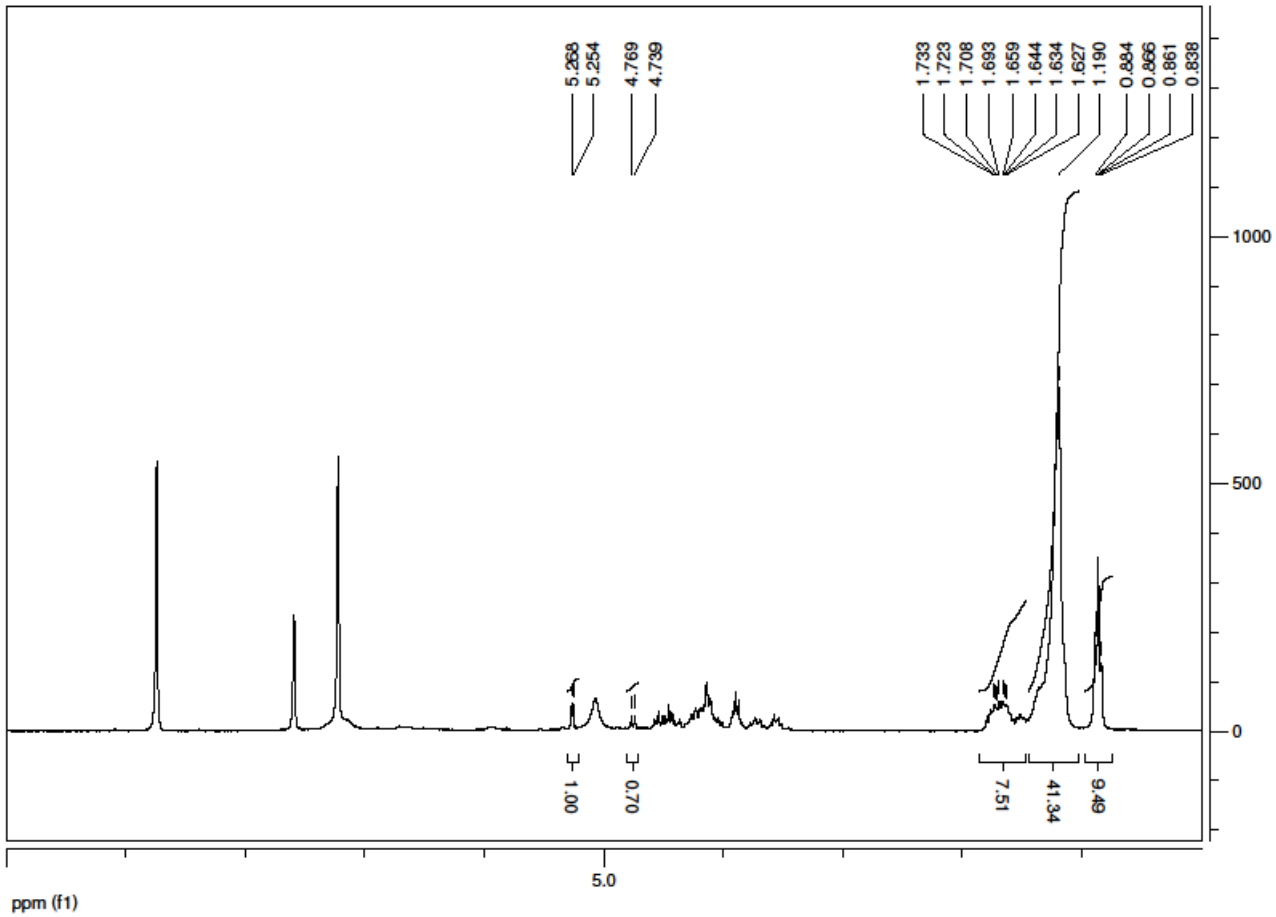


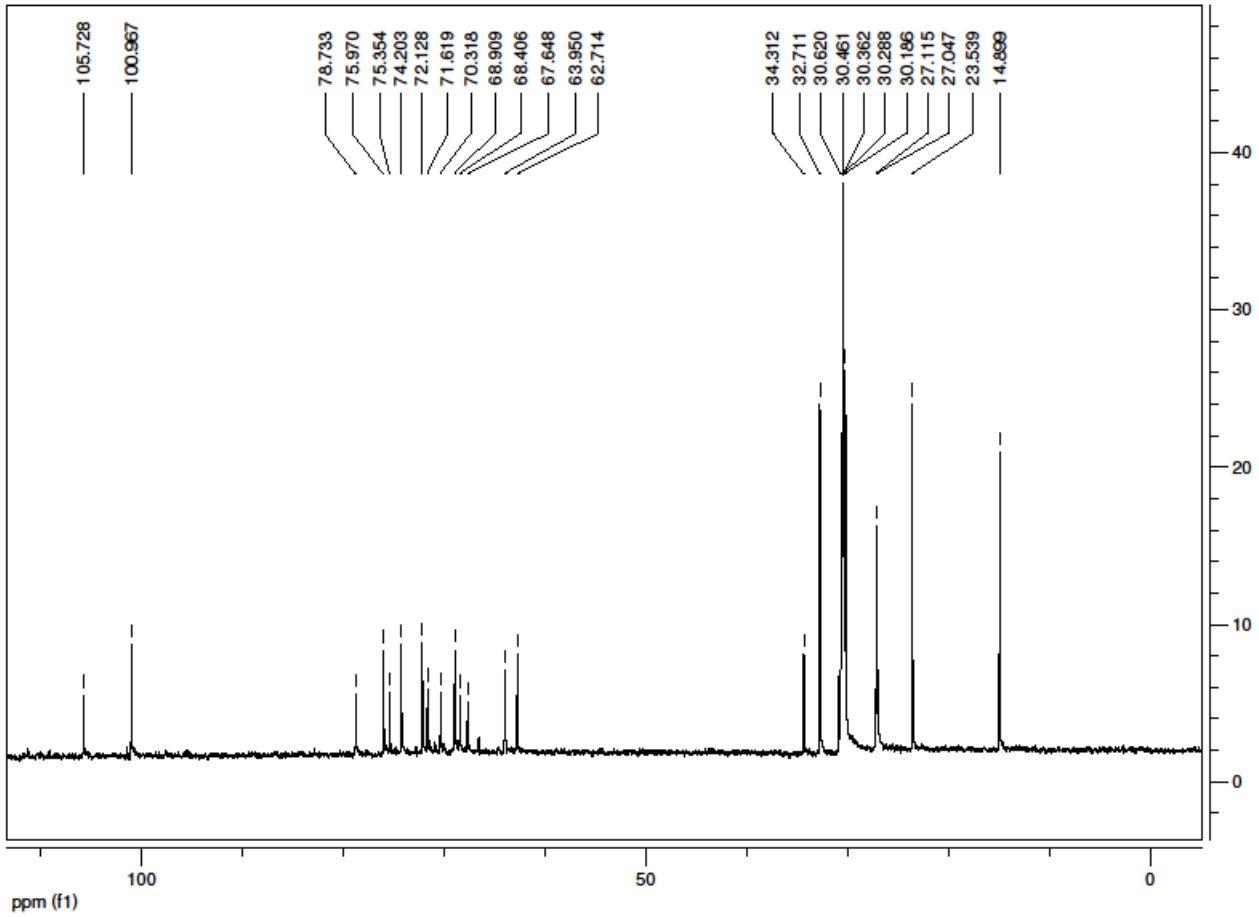




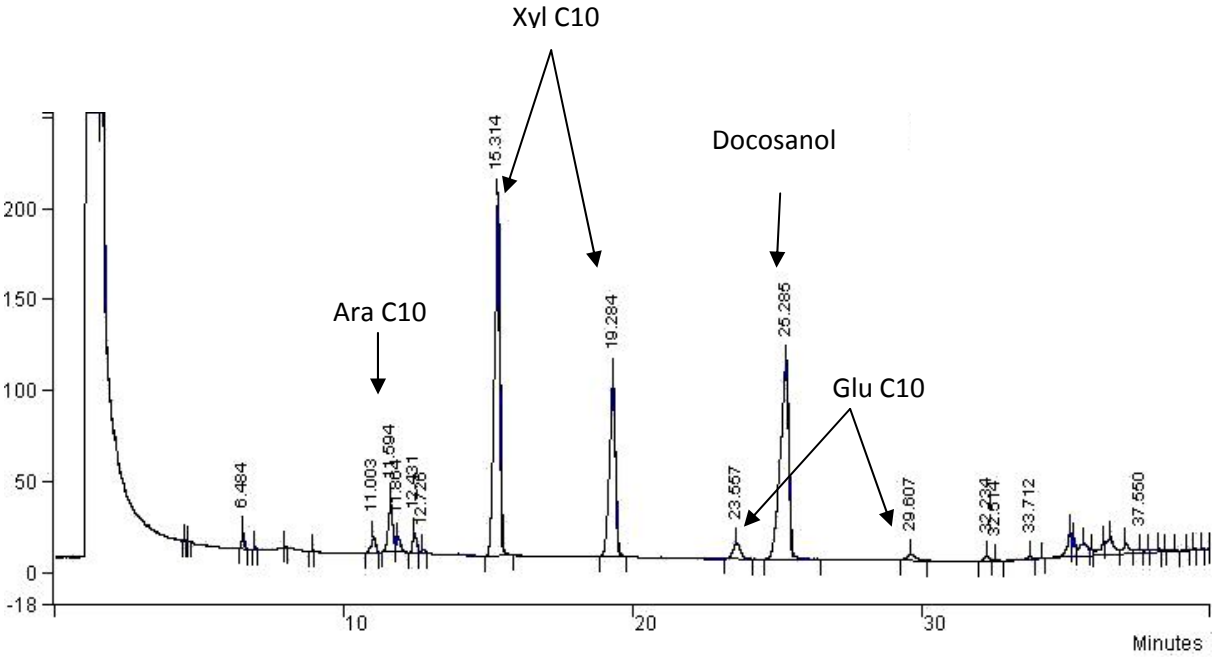
m/z calculated for trimethylsilylated standard [$C_{28}H_{64}O_6Si_4$ +], 608.38, found 608

NMR spectra of the isolated decyl-glycosides crude mixture obtained from wheat bran (Entry 9, Table 1).




105.728
100.967
78.733
75.970
75.354
74.203
72.128
71.619
70.318
68.909
68.406
67.648
63.950
62.714
34.312
32.711
30.620
30.461
30.362
30.288
30.186
27.115
27.047
23.539
14.899
40
30
20
10
0
100
50
0
ppm (f1)

Trace GC of the crude glycosides mixture (table 1 entry 12) after trimethylsilylether formation[1].



Materials: docosanol, anhydrous pyridine (ACROS, 99 +%), 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (ACROS, 98%), Chlorotrimethylsilane (TMSCl) (Aldrich, 98%), Tert-butylméthyléther (TBME), (ACROS, 99%)

PREPARATION OF THE SAMPLE

In a 50 ml flask, weigh accurately 1000 mg of glycosides, add precisely 100 mg of docosanol. Add 10 ml of anhydrous pyridine and let the material solubilize for 12 hours under magnetic stirring.

When dissolved, add 5 ml of HMDS and 3 ml of TMSCl. Let the mixture under magnetic stirring during 10 minutes. Evaporate the solvent under vacuum 1mbar at 55 ° C. The crude residue is then solubilized in 6 ml of TBME and filtered.

GAS CHROMATOGRAPHY:

* Apparatus: Shimadzu GC-14B / * Column: Track 2 CP-sil 13 CB (Varian) Inside diameter: 0.32 mm; Thickness: 1.2 m; Length: 25 m / * Chromatographic conditions: File 7, Range 0;

Oven: 230 ° C: 32 min; 20 ° C / min, 300 ° C; 300 ° C: 5min; - Injector: 250 ° C - Sensors (F.I.D.): 340 ° C

* Injection: 0.4 µl

* Carrier gas: Helium 100 kPa

STANDARD CALIBRATION

ETALONNAGE DP1 ARA,XYL, GLU DE C8 à C14 PAR RAPPORT AU C22OH :

2001 + pt 2004 + pt 2006 :

Etalon interne		a	b		R2
C22	ARA C8	1,6238	-0,0363	0,13<Ra<1,4	**0,991**
C22	XYL C8	1,7455	0,0033	0,10<Ra<0,65	**0,9985**
C22	GLU C8	1,0481	0,0520	0,3<Ra<2,70	**0,9938**
C22	ARA C10	1,2951	-0,0021	0,2<Ra<0,92	**0,9947**
C22	XYL C10	1,8945	-0,0475	0,10<Ra<1,05	**0,9958**
C22	GLU C10	1,0215	-0,0183	0,28<Ra<2,60	**0,9973**
C22	ARA C12	1,2137	0,0492	0,15<Ra<0,76	**0,9881**
C22	XYL C12	1,0250	0,0107	0,05<Ra<1,1	**0,9981**
C22	GLU C12	1,0630	0,0063	0,2<Ra<0,72	**0,9969**
C22	ARA C14	1,2503	0,0042	0,16<Ra<0,86	**0,9967**
C22	XYL C14	0,9651	0,0256	0,07<Ra<1,1	**0,9966**
C22	GLU C14	0,9079	0,0839	0,22<Ra<1,22	**0,9665**