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A MONOACYL GALACTOSYLGLYCEROL FROM *SONCHUS ARVENSIS*

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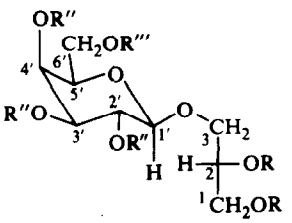
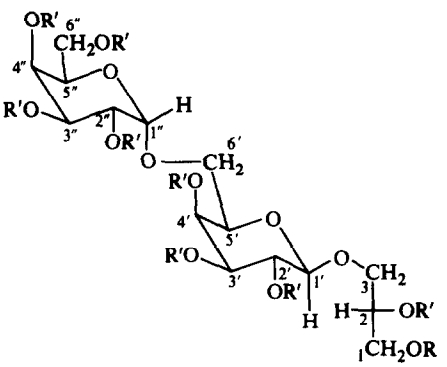
Key Word Index—*Sonchus arvensis*; Compositae; glycosylglycerides; 1-linolenyl-3-*O*-β-D-galactopyranosyl-*sn*-glycerol

Abstract—The major lipids isolated in a phytochemical study of *Sonchus arvensis* were 1,2-dilinolenyl-3-*O*-β-D-galactopyranosyl-*sn*-glycerol, 1,2-dilinolenyl-3-*O*-(α-D-galactopyranosyl-(1 → 6)-*O*-β-D-galactopyranosyl-*sn*-glycerol and the previously undescribed 1-linolenyl-3-*O*-β-D-galactopyranosyl-*sn*-glycerol.

INTRODUCTION

Sesquiterpene lactones have been isolated from several *Sonchus* species [1]. As part of our search for biologically active lactones we have now examined *Sonchus arvensis* L. Lactones were not found, but the herbaceous parts of fresh plant material furnished a lipid fraction consisting of the diacyl galactosylglycerol, **1a**, the monoacyl galactosylglycerol, **1c**, and the diacyl digalactosylglycerol, **2a**, each





1a R,R′=linolenyl,R″,R‴=H
1b R,R′=linolenyl,R″,R‴=Ac
1c R=linolenyl,R′,R″,R‴=H
1d R=linolenyl,R′,R″,R‴=Ac
1e R,R′,R″,R‴=H
1f R,R′,R″,R‴=Ac
1g R,R′=stearyl,R″,R‴=H
1h R,R′=stearyl,R″,R‴=TMS
1i R,R′=stearyl,R″,R‴=Ac
1j R,R′=stearyl,R″=H,R‴=trityl
1k R,R′=stearyl,R″=Ac,R‴=trityl
1l R=stearyl,R′,R″,R‴=H
1m R=stearyl,R′,R″,R‴=TMS
1n R=stearyl,R′,R″,R‴=Ac
1o R=stearyl,R′,R″=H,R‴=trityl
1p R=stearyl,R′,R″=Ac,R‴=trityl
1q R=stearyl,R′R″,R‴=Me

2a R=linolenyl,R′=H
2b R=linolenyl,R′=Ac
2c R,R′=H
2d R,R′=Ac
2e R=stearyl,R′=H
2f R=stearyl,R′=Ac

essentially uncontaminated by acyl glycosylglycerols derived from other fatty acids. While **1a** and **2a** are widely distributed in plants, generally as components of complex mixtures [2, 3], **1c** has not been described previously. Earlier examinations of *S. arvensis* resulted in the isolation of triterpenes [1], mannitol [1] and various flavonoids [1, 4–6]; a study of the oil has also been reported [7, 11].

RESULTS AND DISCUSSION

Column chromatograhy of the methanol extract of fresh plant material (the yields with chloroform were lower due to decomposition) gave, in order of polarity, apparently homogeneous **1a**, **1c** and **2a** in proportions which varied somewhat with time of collection (see Experimental). Evidence that **1c** is not an artefact produced by an endogenous acyl hydrolase in the course of extraction is given in the Experimental. Catalytic hydrogenation converted these relatively unstable substances to stable **1g** [5], **1l**, and **2e** [5] which were characterized as the tetra-acetate, **1i**, the penta-acetate, **1n** and the hepta-acetate, **2f** (for ^{1}H NMR spectra, see Table 1). Hydrolysis (potassium hydroxide, ethanol) of **1a**, **1c** and **2a** followed by acidification and methylation with diazomethane gave methyl linolenate, identified by ^{1}H NMR spectrometry and GC; hydrolysis (potassium hydroxide, ethanol) of **1g**, **1l** and **2c** gave stearic acid. Hydrolysis of **1a** and **1c** (potassium carbonate, methanol, water) gave, in addition to linolenic acid and methyl linolenate, a substance which had properties (mp, rotation) similar to those given for 3-*O*-*β*-D-galactopyranosyl-*sn*-glycerol (**1e**) [8–10]. Hydrolysis of **2a** in the same fashion gave linolenic acid, methyl linolenate and a substance which had properties similar to those of 3-*O*-(α-D-galactopyranosyl-(1 → 6)-*O*-*β*-D-galactopyranosyl)-*sn*-glycerol (**2c**) [8–10]. Acid hydrolysis of **1e** and **2c** gave galactose.

Acetylation converted **1e** and **2c** to the hexa-acetate, **1f**, and the nona-acetate, **2d**, analysis of whose ^{1}H NMR spectra (Table 1) confirmed the above structure assignments. All frequencies were assigned by decoupling experiments. In **1f**, C-1′ of the galactose unit in the *β*-configuration (*δ*H-1′ 4.49*d*, $J_{1',2'}$ = 8 Hz) was clearly

Table 1. ^{1}H NMR data for compounds **1f**, **1h**, **1i**, **1m**–**1p** and **2d** (270 MHz, $CDCl_3$, TMS as int. standard)*

	1f	**1h**†	**1i**†	**1m**‡	**1n**‡	**1p**§	**2d**‖
H-1a	4.31 *dd* (12, 4)	4.38 *dd* (12, 4)	4.31 *dd* (12, 3.5)	4.23 *dd* (12, 4)	4.31 *dd* (12, 4)	4.31 *dd* (12.5, 3)	4.31 *dd* (12, 3.5)
H-1b	in 4.15 *m* (3)	4.19 *dd* (12, 6.5)	in 4.15 *m* (3H)	in 4.02 *m*	in 4.15 *m* (3H)	4.03 *dd* (12, 6)	4.15 *m*
H-2	5.19 *m*	5.21 *q*	5.19 *m*	in 4.02 *m* (2H)	in 5.19 *m* (2H)	5.12 *m*	in 5.19 *m* (2p)
H-3a	3.70 *dd* (11, 5.5)	in 3.62 *m* (4H)	3.68 *dd* (11, 5)	3.47 *dd* (11, 7)	3.70 *dd* (11, 5.5)	3.61 *dd* (11, 5.5)	3.68 *dd* (10.5, 3.5)
H-3b	3.96 *dd* (11, 5)	3.96 *dd* (11, 4.5)	3.95 *dd* (11, 5)	3.77 *dd* (11, 3.5)	3.96 *dd* (11, 5)	3.91 *dd* (11, 5.5)	3.98 *dd* (10.5, 5)
H-1′	4.49 *d* (8)	4.14 *d* (7.5)	4.48 *d* (8)	4.14 *d* (7.5)	4.49 *d* (8)	4.42 *d* (7)	4.50 *d* (8)
H-2′	5.19 *dd* (10.5, 8)	in 3.62 *m* (4H)	5.19 *dd* (10.5, 8)	in 3.62 *m* (3H)	in 5.19 *m* (2H)	5.07 *dd* (11, 8)	in 5.19 *m*
H-3′	5.02 *dd* (10.5, 3)	3.38 *m* (2H)	5.01 *dd* (10.5, 3.5)	3.38 *m* (2H)	5.02 *dd* (10.5, 3)	5.01 *dd* (10.5, 3)	5.02 *dd* (10.5, 3.5)
H-4′	5.39 *brd* (3)	3.83 *brd* (2.5)	5.39 *brd* (3.5)	3.83 *brd* (2.5)	5.39 *brd* (3)	5.53 *brd* (3)	5.43 *brd* (3.5)
H-5′	3.92 *brt* (6)	in 3.62 *m* (4H) or	3.90 *brt* (6)	in 3.62 *m* (3H) or	3.92 *brt* (6)	3.76 *brt* (6)	3.87 *brt* (6)
H-6′	in 4.15 *m*	3.38 *m* (2H)	in 4.15 *m* (3H)	3.38 *m* (2H)	in 4.15 *m* (3H)	3.35 *dd*	4.10 *m*
H-6′b	in 4.15 *m* (3H)					3.07 *dd* (9.5,8)	
Ac	2.16, 2.07 2.06, 2.06 2.05, 1.98	—	2.15, 2.06 2.04, 1.98		2.16, 2.06 2.06, 2.05 1.98	2.03, 2.01 1.90, 1.88	2.13, 2.13 2.08, 2.07 2.07, 2.06 2.06, 1.97 1.97

*Coupling constants (Hz) in parentheses.

†Stearate, 2.29 *t* (7 Hz, 4H), 1.61 *q* (7 Hz, 5H), 1.26 *m* (56H), 0.89 *t* (7 Hz, 6H)

‡Stearate, 2.31 *t* (7 Hz, 2H), 1.62 *q* (7 Hz, 2H), 1.26 *m* (28H), 0.89 *t* (7 Hz, 3H).

§Trityl, 7.37 *m* (15H), stearate, 2.24 *t* (7 Hz, 2H), 1.56 *m* (2H), 1.26 *m* (28H), 0.89 *t* (7 Hz, 3H)

‖Terminal galactose unit: H-1, 4.97 *d* (4), H-2, 5.12 *dd* (11, 4), H-3, 5.30 *dd* (11, 3.5), H-4, 5.46 *br d* (3.5), H-5, 4.21 H-6a, 3.44 *dd* (10, 6.5), H-6b, 3.79 *dd* (10, 6.5).

attached to C-3 of the glycerol residue as indicated by the chemical shifts of H-1a, H-1b, H-2 and H-3a, H-3b. In **2d**, C-1′ of the central galactose unit, also in the β-configuration ($J_{1',2'} = 8$ Hz), was again attached to C-3 of the glycerol moiety and linked to α-configurated C-1″ of the terminal galactose unit (δ4.97*d*, $J = 4$ Hz), via C-6′ because of the chemical shifts of H-2′, H-3′, H-4′ and H-5′ which had remained the same as in **1f**.

Comparison of the ^{1}H NMR spectra of **1f**, **1i** and **1n** with the spectra of the TMS derivatives **1h** and **1m** (Table 1) showed that **1i** and **1n** contained two stearyl residues (as did the TMS ether of **2c**) and **1b** and **1m** only one; that the two stearyl residues of **1i** (and of **2c**) were attached to C-1 and C-2 of the glycerol half and that the single stearyl residue of **1n** was either on C-1 of the glycerol or C-6′ of the galactose moieties, most probably on C-1 of the former. In an attempt to settle this ambiguity, **1l** was tritylated to **1o** and subsequently acetylated to give the monotrityl tetra-acetyl derivative **1p**. Comparison of the ^{1}H NMR spectrum of **1p** (Table 1) with that of **1h** and **1m** suggested that the new trityl group was on C-6′ and hence that the stearyl residue was on C-1. Finally, methylation of **1l** (sodium hydride, DMSO, methyl iodide) to **1q** followed by acid hydrolysis gave stearic acid and 2,3,4,6-tetra-methylgalactose identical with authentic material. Hence, the structure of the new monolinolenate was 1-linolenyl-3-*O*-β-D-galactopyranosyl-*sn*-glycerol (**1c**).

EXPERIMENTAL

Extraction of Sonchus arvensis. *S. arvensis* was harvested on the RDL campus in Jan–June 1981 (NPCD/4/81), Jul–Aug (NPCD/6/81) and Sep–Dec (NPCD/6/81). Above ground parts (2.4 kg), collected during the first period, were macerated while still fresh and extracted with MeOH (5 l.) at room temp. Most of the MeOH was removed at red. pres.; the residue, mainly aq. but containing a small amount of MeOH, was extracted with petrol (60–80°) (6 × 100 ml) and then with $CHCl_3$ (5 × 100 ml). The $CHCl_3$ extract was dried and concd at red. pres. and the gummy residue (10.5 g) was chromatographed over 200 g Si gel (60–120 mesh, BDH, India) packed in $CHCl_3$, 150 ml fractions being collected in the following order: fractions 1–5 ($CHCl_3$), 6–10 ($CHCl_3$–MeOH, 99:1), 11–15 ($CHCl_3$–MeOH, 49:1), 16–20 ($CHCl_3$–MeOH, 97:3), 21–25 ($CHCl_3$–MeOH, 19:1), 26–30 ($CHCl_3$–MeOH, 9:1), 31–35 ($CHCl_3$–MeOH, 17:3), 36–40 ($CHCl_3$–MeOH, 4:1), 41–45 ($CHCl_3$–MeOH, 1:1) and 46–50 (MeOH).

Fractions 17–20 each showed one major spot on TLC and were combined. Purification by prep. TLC ($CHCl_3$–MeOH, 9:1) gave 0.35 g **1a** as a gum, $[\alpha]_D$ +26° (MeOH), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1735, 1650 (w) 1615 (w), 1200, 1030, 950; UV λ_{max}^{MeOH} nm: 275, 260, 255, 250, 235. The material decomposed at room temp. but was reasonably stable when stored in MeOH soln. The only significant peak in the EIMS was at *m/z* 261 corresponding to $C_{17}H_{29}O^+$. Acetylation of 20 mg **1a** with 0.5 ml pyridine and 1 ml Ac_2O at room temp. overnight, work-up in the usual fashion and prep. TLC (EtOAc–C_6H_6, 1:3) of the crude product gave 20 mg **1b** as a gum, IR ν_{max} cm^{-1}: 1735, 1200 and 1050.

Fractions 26–30 showed one major spot and were combined. Purification by prep. TLC ($CHCl_3$–MeOH, 4:1) gave 0.7 g **1c** as a gum, $[\alpha]_D$ +13° (MeOH) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1735, 1650 (w), 1615 (w), 1230, 1050, 975 and 925; UV λ_{max}^{MeOH} nm: 274, 265, 255 and 228. The material also decomposed at room temp. but was stable in MeOH soln. Acetylation of 30 mg **1c** and prep. TLC of the crude product (EtOAc–C_6H_6, 1:4) gave 30 mg **1d** as a gum, IR ν_{max} cm^{-1}: 1735, 1230 and 1050.

Fractions 32–35 each of which exhibited one major spot were combined. Purification by prep. TLC ($CHCl_3$–MeOH, 4:1) gave 0.12 g **2a** as a gum which decomposed at room temp. but could be stored in MeOH soln, $[\alpha]_D$ +67° (MeOH), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1735, 1650 (w), 1600 (w) and 1075. Acetylation of 35 mg **2a** and purification of the crude product by prep. TLC (EtOAc–C_6H_6, 1:3) gave 32 mg **2b** as a gum, IR ν_{max} cm^{-1}: 1735, 1200 and 1050.

Extraction of dried plant with MeOH gave no acyl glycosylglycerols. When the fresh plant was extracted with $CHCl_3$, it was difficult to obtain **1a**, **1c** and **2a** by CC due to decomposition. That **1c** was not an artefact formed by enzymatic hydrolysis was shown as follows. (a) The fresh plant without homogenization or grinding was boiled within 10 min of harvest with MeOH for 15 min. Evaporation of MeOH and purification over Si gel followed by prep. TLC gave material containing 52% of **1a**, 23% of **1c** and 25% of **2a**. Extraction of the same fresh plant with $CHCl_3$ for 15 min gave material also containing 52% **1a**, 23% **1c** and 25% **2a**, but the total yield was *ca* 80% of the yield from MeOH. (b) The fresh plant was ground with EDTA, extracted with MeOH and analysed as before giving 50% **1a**, 25% **1c** and 25% **2a**. (c) Breaking the stem of a fresh plant by hand produced a bitter latex which on TLC was found to contain **1a**, **1c** and **2a** in about the same concn as obtained by MeOH extraction.

Seasonal variations in the composition of acyl glycosylglycerol content were as follows. Plants harvested from Jan. to Jun. gave an acyl glycosylglycerl fraction containing *ca* 30% **1a**, 60% **1c** and 10% **2a**; plants harvested in Jul. and Aug. *ca* 40% **1a**, 30% **1e** and 30% **2a**, and plants harvested from Sep. to Dec. *ca* 50% **1a**, 25% **1c** and 25% **2a**.

Hydrolyses of **1c**. (a) A soln of 61 mg **1c** in 4 ml 5% ethanolic KOH was refluxed (N_2 atmosphere) for 30 min at which time TLC (EtOAc–C_6H_6, 1:1) indicated the disappearance of the starting material. The reaction mixture was neutralized with HOAc and extracted with Et_2O. Esterification of the washed and dried extract (30 mg), with CH_2N_2 gave methyl linolenate, IR ν_{max} cm^{-1}: 1725, 1665; MS 292 $[M]^+$ 261, identified by NMR spectrometry (270 MHz, $CDCl_3$): δ5.36 (60H, *br*, vinyl Hs), 3.66 (OMe), 2.81 (4H, *t*, $J = 5$ Hz, H-11 and H-13), 2.29 (2H, *t*, $J = 7$ Hz, H-2), 2.06 (4H, *m*, H-8 and H-17), 1.62 (2H, *q*, $J = 7$ Hz, H-7?), 1.31 (8H, *br*, 4 × –CH_2–), 0.98, (3H, *t*, $J = 7$ Hz, H-18); and by GC comparison with an authentic sample.

(b) A mixture of 100 mg **1c** in 3 ml MeOH and 5 ml 1% aq. K_2CO_3 soln was refluxed with stirring (N_2 atmosphere) for 25 min at which time TLC (EtOAc–C_6H_6, 1:1) indicated the disappearance of the starting material. Dilution with H_2O, acidification with HOAc and extraction with $CHCl_3$ (4 × 50 ml) gave, after washing and drying of the extract, a fraction which showed two spots on TLC (C_6H_6–EtOAc) identified as linolenic acid (39 mg) and methyl linolenate (29 mg). The aq. layer was further extracted with *n*-BuOH (4 × 20 ml). Evaporation of the extract at red. pres. and purification of the residue by prep. TLC ($CHCl_3$–MeOH, 7:3) gave 30 mg 3-*O*-β-D-galactopyranosyl-*sn*-glycerol (**1e**) as a semi-solid material which after recrystallization had mp 138–140°, $[\alpha]_D$ +6.2° (H_2O; *c* 0.74); lit. mp 139–140°, $[\alpha]_D$ +3.77° (H_2O) [7]. Acetylation of 36 mg of this material and prep. TLC (C_6H_6–EtOAc, 2:1) of the crude product gave 32 mg **1f**, $[\alpha]_D$ +0.62° ($CHCl_3$; *c* 0.4). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1200, 1050; MS *m/z*: 331 $[M-59]^+$ 271, 229, 221, 200, 169, 115, 99; ^{1}H NMR: Table 1; ^{13}C NMR: C=O at δ17046, 170.32, 170.13, 170.02 (2) and 169.31 C-1′ doublet at δ101.54, methine doublets at δ70.84, 70.74, 69.89, 68.62 and 66.98, methylene triplets at δ67.50 (C-1), 62.45 (C-3) and 61.25 (C-6′), methyl quartets at δ20.89, 20.63 (4) and 20.54.

Hydrolysis of 50 mg **2a** with K_2CO_3 gave 20 mg linolenic acid, 20 mg methyl linolenate and from the *n*-BuOH extract, 14 mg 3-*O*-

(α-D-galactopyranosyl(1 → 6)-*O*-β-D-galactopyranosyl)-*sn*-glycerol (**2c**), mp 184–186°, $[\alpha]_D$ +82° (H_2O; *c* 0.80), lit. [7] 182–184°, $[\alpha]_D$ +86° (H_2O), after purification by prep. TLC ($CHCl_3$–MeOH, 3:2). Acetylation of 30 mg **2c** and purification of the crude product by prep. TLC (C_6H_6–EtOAc, 2:1) gave 29 mg **2d** as a gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1200 and 1050; $[\alpha]_D$ +60.4° ($CHCl_3$; *c* 0.39); ^1H NMR: Table 1; ^{13}C NMR: C=Os at δ170.57, 170.52, 170.35, 170.13 (2), 170.00 (2), 169.92 and 169.38. C-1′ doublet at δ101.59, C-1″ doublet at δ96.69, methine doublets at δ71.68, 70.91, 69.88, 68.68, 67.96, 67.56, 67.45 (2) and 66.64, methylene triplets at δ67.26 (C-1), 65.63 (C-6′), 62.50 (C-3) and 61.60 (C-6″), methyl quartets at δ20.87, 20.65 (4) and 20.60 (4).

Hydrolysis of **1e**. A soln of 50 mg **1e** in 70 ml 1 N H_2SO_4 was reluxed for 1 hr until TLC ($CHCl_3$–MeOH, 7:3) indicated completion of the reaction. The mixture was diluted with H_2O, neutralized with K_2CO_3 and extracted with *n*-BuOH. Evaporation of the washed and dried extract and prep. TLC ($CHCl_3$–MeOH, 7:3) of the residue gave 27 mg of solid which was recrystallized from H_2O to give galactose, mp 118–119°, identified by TLC comparison with authentic material and mmp. Acetylation gave galactose penta-acetate as a gum, identical by TLC comparison with authentic galactose penta-acetate.

Hydrogenation of **1a** *and* **1c**. (a) A soln of 100 mg **1c** in 25 ml EtOH was hydrogenated with 100 mg PtO_2 catalyst for 2 hr at atmospheric pres. Filtration and removal of the solvent at red. pres. gave a quantitative yield of **1l** which, after recrystallization from MeOH–$CHCl_3$, had mp 108–110° with a meniscus forming at 140–142°, IR ν_{max}^{nujol} cm^{-1}: 3400, 1735, 1170 and 1050; ^1H NMR (TMS ether **1m**): Table 1. Acetylation of 38 mg **1l** followed by prep. TLC of the crude product (C_6H_6–EtOAc, 4:1) gave 36 mg of gummy **1n**, $(\alpha)_D$ −1.1° ($CHCl_3$; *c* 0.32); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1225 and 1050; ^1H NMR: Table 1. Reaction of 85 mg **1l** in 1 ml pyridine with 250 mg trityl chloride by warming until dissolved followed by standing overnight at room temp. indicated complete disappearance of starting material. Dilution with 50 ml H_2O, extraction with $CHCl_3$ (4 × 50 ml) and evaporation of the washed and dried extract at red. pres. gave crude **1o**; an attempt to purify this by prep. TLC (EtOAc–C_6H_6, 1:1) resulted in isolation of only 10 mg pure **1o** as a gum and recovery of 70 mg **1l** due to hydrolysis of **1o** on the TLC plate. Acetylation of 10 mg **1o** with 0.5 ml pyridine and 1 ml Ac_2O overnight at room temp. followed by the usual work-up and prep. TLC (C_6H_6–EtOAc, 9:1) gave 10 mg **1p** which was stable. The ^1H NMR spectrum is listed in Table 1.

(b) Hydrogenation of 120 mg **1a** in 25 ml EtOH as described for **1c** gave 120 mg **1g**, mp 118–120° with a meniscus forming at 150–152° [9] after recrystallization from MeOH–$CHCl_3$, IR ν_{max}^{nujol} cm^{-1}: 3500, 1735, 1230, 1175 and 1050; ^1H NMR (TMS ether **1h**): Table 1. Acetylation of 50 mg **1g** in the usual way followed by prep. TLC of the crude product C_6H_6–EtOAc, 4:1) gave 48 mg **1i**, mp 56–58° after crystallization from MeOH; $[\alpha]_D$ −1.4° ($CHCl_3$; *c* 0.57); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1230 and 1050; ^1H NMR: Table 1. Conversion of 50 mg **1g** to the trityl ether in the manner described for **1l** gave crude **1j**; attempted purification by prep. TLC (EtOAc–C_6H_6, 1:1) gave 20 mg **1j** and 30 mg of recovered **1g**. Acetylation of 15 mg **1j** in the usual fashion and prep. TLC (C_6H_6–EtOAc, 9:1) of the crude product gave 15 mg **1k**.

Reactions of **1l**. (a) A soln of 60 mg **1l** in 6 ml 5% ethanolic KOH was refluxed (N_2 atmosphere) for 30 min at which time TLC indicated complete disappearance of the starting material. Neutralization with HOAc and extraction with $CHCl_3$ followed by evaporation of the washed and dried extract gave 28 mg stearic acid, mp 69–69.5° after crystallization from EtOH, identical with authentic stearic acid by TLC comparison and mmp. Hydrolysis of 80 mg **1g** in the same manner gave 34 mg stearic acid.

(b) To a soln of 143 mg **1l** in 1.5 ml DMSO was added 80 mg NaH. After stirring for 30 min at room temp. (N_2 atmosphere) 5 ml MeI was added and stirring was continued for 3 hr at which time TLC ($CHCl_3$–MeOH, 4:1) indicated complete disappearance of the starting material. The mixture was poured into ice H_2O and extracted with $CHCl_3$. The combined extracts were washed with H_2O, dried and evaporated; prep. TLC of the residue (C_6H_6–EtOAc, 2:1) gave 52 mg gummy **1q** whose IR and ^1H NMR spectrum indicated methylation of all hydroxyl groups; IR ν_{max} cm^{-1}: 1735 and 1050; ^1H NMR very strong signal at δ3.65 (approx 15H) superimposed on the signals of **1h**. A soln of 50 mg **1q** in 4 ml HOAc and 4 ml 4 N HCl was refluxed for 45 min at which time TLC (C_6H_6–EtOAc, 1:1) indicated complete disappearance of the starting material. Neutralization with $PbCO_3$, dilution with H_2O, extraction with $CHCl_3$ and evaporation of the washed and dried extract at red. pres. followed by prep. TLC (EtOAc–C_6H_6, 4:1) gave stearic acid as the less polar fraction; the MS of the gummy more polar fraction (10 mg), had $[M]^+$ at *m/z* 236 for a galactose tetramethyl ether. Other significant peaks were at *m/z* 218, 172 and 101. The material was identical with authentic 2,3,4,6-tetramethylgalactose on TLC. Acetylation of 12 mg of this hydrolysate in the usual manner and prep. TLC (C_6H_6–EtOAc, 2:1) of the crude product gave 12 mg galactose tetramethyl ether monoacetate, MS *m/z* 278 $[M]^+$ 218 $[M - HOAc]^+$.

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