H_2O produced **11** in 81% overall yield (from **9**).

The Hydrochloride of **11**: A small portion of **11** was dissolved in an excess of 10% (w/w) ethanolic HCl, and dry ether was added. The resulting precipitate was filtered off and recrystallized from acetone–EtOH (1: 1, v/v) to yield the hydrochloride as colorless scales, mp 249—251°C (dec.) (dried over P_2O_5 at 2 mmHg and room temp. for 20 h); IR ν_{max}^{Nujol} cm^{-1}: 2510 (NH^+), 1715 (Me_2CO contained); NMR (Me_2SO-d_6) δ: 0.92 (9H, s, Me_3C), 2.08 (2H, 1/3 Me_2CO), 3.75 (6H, s, two MeO's), 4.22 (1H, dull d-d, $H_{(11b)}$), 6.78 and 6.85 (1H each, s, aromatic protons), 10.8 (1H, b, NH^+). *Anal.* Calcd for $C_{19}H_{30}ClNO_2 \cdot 1/3CH_3COCH_3$: C, 66.86; H, 8.98; N, 3.90. Found: C, 66.85; H, 9.11; N, 3.97.

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Legume Saponins of *Gleditsia japonica* Miquel.[1] III. Further Desmonoterpenyl Glycosides of Echinocystic Acid

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Two triterpenoid saponins, gleditsia saponins E (GS-E) and G (GS-G), were isolated from legumes of *Gleditsia japonica* cv. 'Saponifera' (Leguminosae). These saponins contain monoterpene ester moieties. The desmonoterpenyl compounds, GS-E′ ($C_{69}H_{112}O_{34}$) and GS-G′ ($C_{64}H_{104}O_{30}$), were obtained from them by alkaline hydrolysis with K_2CO_3 and both were identified as echinocystic acid 3,28-O-bisdesmoside on the basis of physical data and degradation products.

Keywords——saponins; bisdesmoside; gleditsia saponin E; gleditsia saponin G; echinocystic acid; *Gleditsia japonica*; Leguminosae

In the preceding paper[1] we reported the isolation of the major saponin, gleditsia saponin C (GS-C), from the legume of *Gleditsia japonica* cv. 'Saponifera,' and the structure elucidation of the desmonoterpenyl compound GS-C′, which was obtained from GS-C by alkaline hydro-

lysis with 5% potassium carbonate. Shibata *et al.* reported[2] the structure elucidation of the monoterpenes attached to GS–C′.

This paper describes the isolation of gleditsia saponins E (GS–E) and G (GS–G), which are minor saponins of *G. japonica* cv. 'Saponifera,' and the structure elucidations of the desmonoterpenyl compounds, GS–E′ (I) and GS–G′ (II), obtained from them by alkaline hydrolysis with 5% potassium carbonate in ethanol.

GS–G′ (II), $C_{64}H_{104}O_{30}$, $[\alpha]_D^{20}$ −35.7° (in methanol), obtained as colorless needles from methanol–water, was hydrolyzed with 2 N sulfuric acid to afford echinocystic acid and three kinds of sugars (glucose, xylose and rhamnose). II was methylated by Hakomori's method[3] to afford the permethylate (III). Its proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed six anomeric proton signals at δ 4.26 (d, J=7 Hz), 4.62 (d, J=7 Hz), 4.69 (d, J=7 Hz), 4.82 (broad s), 5.17 (broad s) and 5.53 (d, J=6 Hz). On methanolysis of III with 1 N hydrogen chloride in dried methanol, six kinds of methylated monosaccharides (methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside, methyl 2,3,4-tri-O-methyl-D-xylopyranoside, methyl 3,4-di-O-methyl-D-glucopyranoside, methyl 2,4-di-O-methyl-D-xylopyranoside, and methyl 2,3-di-O-methyl-L-rhamnopyranoside) were obtained and identified by comparison with authentic samples on thin layer chromatography (TLC) and gas liquid chromatography (GLC). Reductive cleavage of the permethylate (III) with lithium aluminum hydride ($LiAlH_4$) afforded a compound (IV) and a methylated oligosaccharide (V). Compound (IV), $C_{41}H_{70}O_8$, $[\alpha]_D^{15}$ −5.5° (in chloroform), showed an anomeric proton at δ 4.26 (d, J=7 Hz) in the ^{1}H-NMR spectrum. On methanolysis of IV, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside and 16-O-methyl-primulagenin A were obtained and identified. The glucose was deduced to have β-configuration from the coupling constant of the anomeric proton in the ^{1}H-NMR spectrum of IV. The methylated oligosaccharide (V) was identified by TLC, IR and ^{1}H-NMR comparisons with a sample obtained from the per-

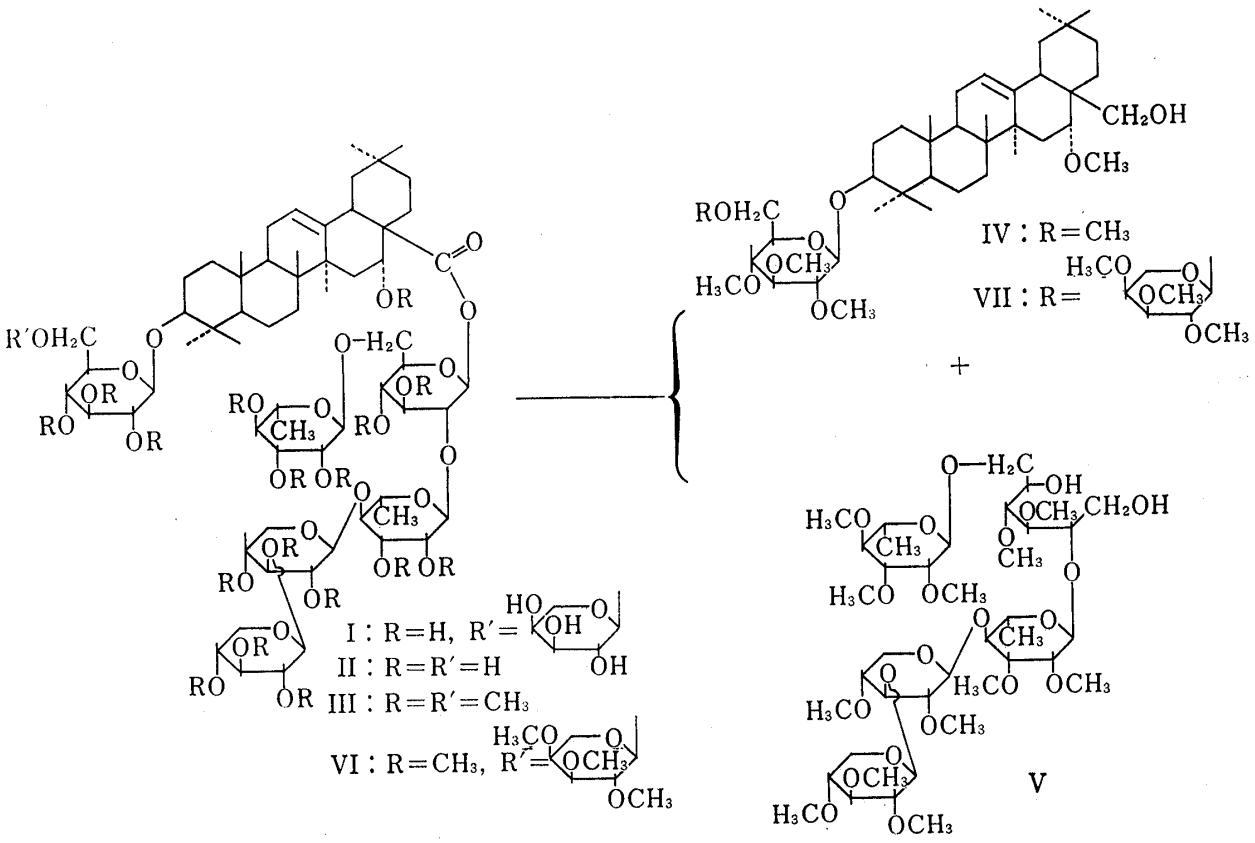

Chart 1

methylate of GS–C by reduction with $LiAlH_4$. Therefore, the desmonoterpenyl compound GS–G′ is established as echinocystic acid 3-O-β-D-glucopyranoside-28-O-[β-D-xylopyranosyl-(1→3)-β-D-xylopyranosyl(1→4)-α-L-rhamnopyranosyl(1→2)][α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside.

GS–E′ (I), $C_{69}H_{112}O_{34}$, $[\alpha]_D^{12}$ −38.0° (in methanol), obtained as colorless prisms from methanol–water, was hydrolyzed with 2 N sulfuric acid to afford echinocystic acid and four kinds of sugars (glucose, arabinose, xylose and rhamnose). I was methylated in the manner described above to afford the permethylate (VI). Its ^{1}H-NMR spectrum showed seven anomeric proton signals at δ 4.17 (d, J=3 Hz), 4.29 (d, J=7 Hz), 4.61 (d, J=7 Hz), 4.70 (d, J=7 Hz), 4.82 (broad s), 5.17 (broad s) and 5.54 (d, J=7 Hz). Reductive cleavage of the permethylate (VI) afforded a compound (VII) and a methylated oligosaccharide (V). Compound (VII), $C_{48}H_{82}O_{12}$, $[\alpha]_D^{10}$ −15.2° (in chloroform) showed two anomeric proton signals at δ 4.29 (d, J=7 Hz) and 4.17 (d, J=3 Hz) in the ^{1}H-NMR spectrum. On methanolysis of VII, methyl 2,3,4-tri-O-methyl-L-arabinopyranoside and methyl 2,3,4-tri-O-methyl-D-glucopyranoside were obtained and identified by comparison with authentic samples (TLC and GLC). The configurations of arabinose and glucose were deduced from the coupling constants of the anomeric protons in the ^{1}H-NMR spectra of VI and VII, and from the molecular rotation differences[4] between II and I.[5] Thus, the structure of the desmonoterpenyl compound GS–E′ is established as echinocystic acid 3-O-[α-L-arabinopyranosyl(1→6)-β-D-glucopyranoside]-28-O-[β-D-xylopyranosyl(1→3)-β-D-xylopyranosyl(1→4)-α-L-rhamnopyranosyl(1→2)][α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside.

Table I. ^{13}C Chemical Shifts (δ) for Carbonyl Carbons and Olefinic Carbons of GS–G, GS–G′, GS–C and Echinocystic Acid Methyl Ester

	GS–G	GS–G′	GS–C	Echinocystic acid methyl ester
1	175.9[a]	176.0[a]	175.9[a] (176.9)	177.6
2	167.2		167.2(168.3)	
3	167.1		167.0(167.8)	
4	146.7		146.8(148.6)	
5	146.4		146.3(145.8)	
6	146.3		146.3(145.8)	
7	144.4[a]	144.4[a]	144.4[a] (145.0)	144.5
8	144.3		144.4(144.6)	
9	132.8		132.8(132.2)	
10	127.6		127.6(128.3)	
11	122.7[a]	122.5[a]	122.8[a] (123.5)	122.6
12	111.8 (two carbons)		111.8(112.6) (two carbons)	

a) These signals are attributable to echinocystic acid moieties.
^{13}C-FT NMR spectra were taken with a Varian CFT-20 NMR spectrometer at 20 MHz in C_5D_5N, with TMS as an internal standard.
The values in parentheses were measured in CD_3OD.

The structures of the monoterpenes attached to GS–G′ were deduced from the ^{13}C-NMR spectrum of GS–G. The spectrum showed the presence of two monoterpene carbonyl carbons at δ 167.2 and 167.1, eight olefinic carbons at δ 146.7, 146.4, 146.3, 144.3, 132.8, 127.6 and 111.8 (two carbons) and two tertiary methyl carbons at δ 28.3 and 28.4. These signals were consistent with the signals of the monoterpene moieties of GS–C. Therefore, it was concluded that GS–G and GS–C carry the same monoterpenes. Studies on the positions of their attachment and on the acyl components of GS–E are in progress.

Experimental

Melting points are uncorrected. The ^{1}H-NMR spectra were measured in $CDCl_3$ with TMS as an internal standard. GLC was carried out on a 200×0.3 cm column of 15% NEGS on Chromosorb W; column temperature 185°C; carrier gas N_2 (30 ml/min).

Isolation and Properties of GS-E and GS-G——The crude saponin fraction was chromatographed on a silica gel column (solvent; $CHCl_3$: MeOH: H_2O=9: 1: 0.1, 8: 3: 1 and 13: 7: 2 in that order). The fraction eluted with the 8: 3: 1 mixture was purified by repeated chromatography on silica gel and gel filtration on Sephadex LH20 (eluted with methanol). The product was repeatedly precipitated from methanol–ether, yielding GS-E as a white powder, mp 191—193°C, $[\alpha]_D^{12}$ −2.9° (c=0.66, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400—3600 (OH), 1725 (COOR). GS-G was a white powder, mp 189—192°C, $[\alpha]_D^{20}$ −16.9° (c=0.93, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3400—3600 (OH), 1725 (COOR).

Hydrolysis of GS-G with 5% K_2CO_3 in EtOH——A mixture of GS-G (30 mg) in EtOH (10 ml) and 5% K_2CO_3 (10 ml) was refluxed for 1 h. The reaction mixture was neutralized with Dowex 50 W×8 under ice cooling, and the neutral solution was concentrated under reduced pressure. The residue was extracted with ether and the aqueous layer was extracted with n-BuOH saturated with water. The organic layer was evaporated to dryness under reduced pressure, and the residue was recrystallized from MeOH–H_2O to afford the desmonoterpenyl compound, GS-G′ (II) as colorless needles. mp 277—279°C, $[\alpha]_D^{20}$ −35.7° (c=0.42 MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400—3500 (OH), 1720 (COOR). *Anal.* Calcd for $C_{64}H_{104}O_{30}\cdot 3H_2O$: C, 54.61; H, 7.88. Found: C, 54.56; H, 7.94.

Hydrolysis of GS-G′ (II) with 2 N H_2SO_4 in EtOH——A solution of II (10 mg) in EtOH (5 ml) was treated with 2 N H_2SO_4 (5 ml) and the mixture was refluxed for 3 h. The solution was concentrated to 5 ml under reduced pressure, diluted with water, and extracted with Et_2O. The aqueous layer was neutralized with Amberlite IR 45 and concentrated to 1 ml. The residue was found to be a mixture of glucose, xylose and rhamnose by PPC and TLC. PPC: solvent, iso-PrOH–H_2O–n-BuOH (7: 1: 2); detection with aniline hydrogen phthalate. TLC: solvent, AcOEt–iso-PrOH–H_2O (32: 12: 6); detection with aniline hydrogen phthalate. The organic layer was washed with water, dried over $MgSO_4$ and evaporated to dryness. The residue was recrystallized from MeOH to give echinocystic acid (2 mg), mp 309—310°C, which was identified by comparison with an authentic sample.[1]

Permethylation of II——According to Hakomori's method, NaH (1 g) was stirred with dimethyl sulfoxide (DMSO, 50 ml) at 90°C for 30 min under N_2 gas. To this reagent (8 ml), a solution of II (120 mg) in DMSO (5 ml) was added, and the whole was stirred for 1 h at room temperature under N_2 gas. CH_3I (12 ml) was added and the whole was stirred for 3 h at room temperature. The reaction mixture was poured into ice-water, and the mixture was extracted with Et_2O. The organic layer was washed with water, dried over $MgSO_4$ and concentrated to afford a syrup (180 mg). This syrup was purified by silica gel column chromatography (solvent; benzene–acetone (9: 1)) to afford the permethylate (III) (100 mg) as a white powder, $[\alpha]_D^{18}$ −45.4° (c=0.69, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: OH (nil), 1725 (COOR). ^{1}H-NMR δ: 0.75—1.30 (27H, m, 9×CH_3), 3.38—3.60 (51H, m, 17×OCH_3), 4.26 (1H, d, J=7 Hz, anomeric H), 4.62 (1H, d, J=7 Hz, anomeric H), 4.69 (1H, d, J=7 Hz, anomeric H), 4.82 (1H, broad s, anomeric H), 5.17 (1H, broad s, anomeric H), 5.53 (1H, d, J=6 Hz, anomeric H). *Anal.* Calcd for $C_{81}H_{138}O_{30}$: C, 61.11; H, 8.74. Found: C, 60.74; H, 8.94.

Methanolysis of III——A solution of III (15 mg) in methanolic 1 N HCl (5 ml) was refluxed for 3 h. The reaction mixture was neutralized with Ag_2CO_3 and filtered. The filtrate was evaporated to dryness and the residue was examined and identified by TLC and GLC comparisons with authentic samples. TLC solvent, benzene–acetone (3: 1); detection with ceric sulfate. GLC t_R values: 1′46″, 2′30″ (methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside), 1′47″, 2′09″ (methyl 2,3,4-tri-O-methyl-D-xylopyranoside), 4′36″, 6′20″ (methyl 2,3-di-O-methyl-L-rhamnopyranoside), 4′37″, 5′54″ (methyl 2,4-di-O-methyl-D-xylopyranoside), 13′25″, 15′20″ (methyl 3,4-di-O-methyl-D-glucopyranoside) and 3′40″, 5′02″ (methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside).

Reduction of III with $LiAlH_4$——The permethylate (III) (80 mg) was dissolved in anhydrous THF (10 ml). $LiAlH_4$ (50 mg) was added, to this solution, and the mixture was refluxed for 2.5 h. The excess $LiAlH_4$ was decomposed with wet ether, and the mixture was extracted with ether and AcOEt, in that order. Each organic layer was washed with water, dried over $MgSO_4$ and evaporated to dryness. The ether extract was purified by preparative TLC with benzene–acetone (5: 2) to afford compound (IV) (25 mg) as a colorless syrup, $[\alpha]_D^{15}$ −5.5° (c=0.98, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH). ^{1}H-NMR δ: 0.83, 0.86, 0.88, 0.90, 0.94, 1.02, 1.25 (3H, each s, 7×CH_3), 3.27, 3.38, 3.51, 3.59, 3.62 (3H, each s, 5×OCH_3), 4.26 (1H, d, J=7 Hz, anomeric H), 5.25 (1H, t, J=3 Hz). *Anal.* Calcd for $C_{41}H_{70}O_8$: C, 71.26; H, 10.21. Found: C, 70.98; H, 10.18. The AcOEt extract was purified by preparative TLC (benzene–acetone (3: 2)) to afford a methylated oligosaccharide (V) (25 mg), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH). ^{1}H-NMR δ: 1.24—1.36 (3H×2, 2×CH_3), 3.45—3.62 (36H, m, 12×OCH_3), 4.64 (1H, d, J=7 Hz, anomeric H), 4.70 (1H, d, J=7 Hz, anomeric H), 4.87 (1H, broad s, anomeric H), 5.05 (1H, broad s, anomeric H), which was found to be identical with a sample obtained by reduction of the permethylate of GS-C.[1]

Methanolysis of IV——A solution of IV in methanolic 2 N HCl was refluxed for 3 h and the reaction mixture was worked up in the same way as for III. Methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside and 16-O-methyl-primulagenin A were identified by comparison with authentic samples.

Hydrolysis of GS-E with 5% K_2CO_3 in EtOH——GS-E (200 mg) was hydrolyzed in the same way as GS-G to give the desmonoterpenyl compound, GS-E′ (I) (120 mg) as colorless prisms from MeOH–H_2O, mp 265—269°C (dec.), $[\alpha]_D^{12}$ −38.0° (c=0.34, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3500—3600 (OH), 1740 (COOR). *Anal.* Calcd for $C_{69}H_{112}O_{34}\cdot 2H_2O$: C, 54.46; H, 7.68. Found: C, 54.69; H, 7.76.

Hydrolysis of GS-E′ (I) with 2 N H_2SO_4 in EtOH——A solution of I (20 mg) in EtOH (10 ml) was treated with 2 N H_2SO_4 (10 ml) and the mixture was worked up in the same way as described for II. Glucose, arabinose, xylose and rhamnose were identified by TLC and PPC, and echinocystic acid was identified by comparison with an authentic sample.

Permethylation of I——Compound (I) (100 mg) was methylated in the same way as II to afford the permethylate (VI) (80 mg), as a white powder, $[\alpha]_D^{10}$ −35.4° (c=0.67, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730 (COOR). ^{1}H-NMR δ: 4.17 (1H, d, J=3 Hz, anomeric H), 4.29 (1H, d, J=7 Hz, anomeric H), 4.61 (1H, d, J=7 Hz, anomeric H), 4.70 (1H, d, J=7 Hz, anomeric H), 4.82 (1H, broad s, anomeric H), 5.17 (1H, broad s, anomeric H), 5.54 (1H, d, J=7 Hz, anomeric H). *Anal.* Calcd for $C_{88}H_{150}O_{34}\cdot 2H_2O$: C, 59.11; H, 8.64. Found: C, 58.85; H, 8.49.

Methanolysis of VI——A solution of VI in methanolic 1 N HCl was worked up in the same way as described for III. GLC t_R values; 2′30″ (methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside), 1′49″, 2′09″ (methyl 2,3,4-tri-O-methyl-D-xylopyranoside), 3′25″ (methyl 2,3,4-tri-O-methyl-L-arabinopyranoside), 4′36″, 6′20″ (methyl 2,3-di-O-methyl-L-rhamnopyranoside), 4′38″, 5′54″ (methyl 2,4-di-O-methyl-D-xylopyranoside), 7′50″, 10′40″ (methyl 2,3,4-tri-O-methyl-D-glucopyranoside), 13′25″, 15′20″ (methyl 3,4-di-O-methyl-D-glucopyranoside). The identities of these products were confirmed by comparison with authentic samples.

Reduction of VI with $LiAlH_4$——The permethylate (VI) (70 mg) was dissolved in anhydrous THF (10 ml), and worked up in the same way as described for III. Compound VII (20 mg) was obtained as a colorless syrup from the ether extract of the reaction mixture, $[\alpha]_D^{10}$ −15.2° (c=0.76, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH). ^{1}H-NMR δ: 0.84, 0.88, 0.90, 0.93, 0.99, 1.03, 1.25 (3H, each s, 7×CH_3), 3.27, 3.44, 3.48, 3.50, 3.56, 3.61, 3.62 (3H, each s, 7×OCH_3), 4.17 (1H, d, J=3 Hz, anomeric H), 4.29 (1H, d, J=7 Hz, anomeric H), 5.24 (1H, triplet-like). *Anal.* Calcd for $C_{48}H_{82}O_{12}\cdot 2H_2O$: C, 64.97; H, 9.77. Found: C, 65.41; H, 9.36. The compound obtained from the AcOEt extract was identical with V as judged by TLC, IR and ^{1}H-NMR comparisons.

Methanolysis of VII——A solution of VII in methanolic 1 N HCl was refluxed for 3 h and the reaction mixture was worked up in the same way as described for III. Methyl 2,3,4-tri-O-methyl-L-arabinopyranoside, and methyl 2,3,4-tri-O-methyl-D-glucopyranoside were identified by TLC and GLC comparisons with authentic samples.

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A Convenient Preparation of N-Acylpyroglutamic Acid

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Pyroglutamic acid reacted with acyl chloride in the presence of triethylamine in acetonitrile, yielding N-acylpyroglutamic acid without epimerization by way of mixed anhydride formation followed by intramolecular N-acylation.