계면활성제

Applications :

섬유공업 27.3%, 고무,플라스틱 공업 10.1%, 토목,건축 8.5%, 식품 8.0%, 의약 화장품 6.5%, 금속, 광업 5.5%, 펄프, 제지 5.3% 농림업 1.9%

기술 개발 방향:

1) 기존 계면활성제를 사용한 새로운 계면활성제 system 개발
2) 생태계를 고려한 고분해성 계면활성제 개발 및 적극적 분해기술 확립
3) 새로운 생체유래 계면활성제 개발과 화학적 변형 생성물 고안 (생체시스템과의 친화성, safety 및 환경오염방지)

생체 계면활성제의 응용

Biosurfactant

정 의 :

"천연물을 기질로 하여 미생물이나 enzyme의 작용에 의하여 생성된 양친매성 화합물"

발 견:

1960년대 후반: 탄화수소를 발효원료로 한 "석유발효" 연구도중 미생물이, 다량의 계면활성 물질을 생산한다는 사실이 밝혀짐

현재까지 연구결과 :

지금까지 약 300여종 이상의 다양한 구조의 생계면활성제가 보고되고 있음

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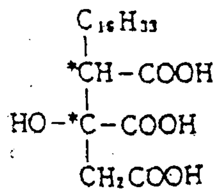
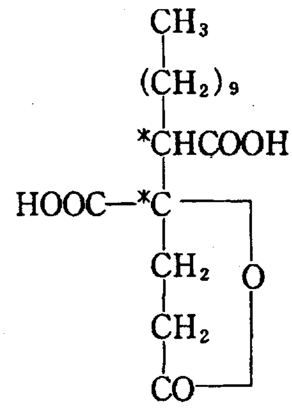
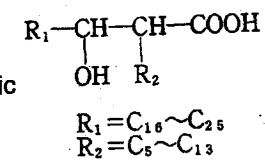
Biosurfactants containing carboxylic acid

Agaricic acid





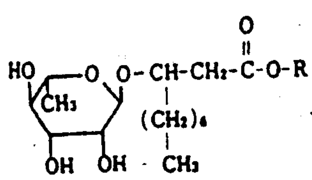
Spiculiosporic acid

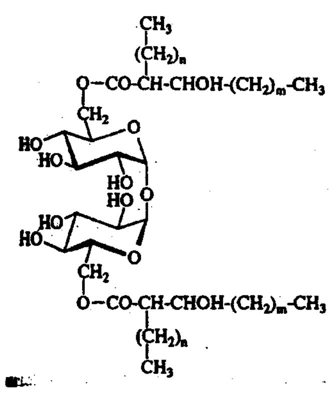


Corynomycolic aicd

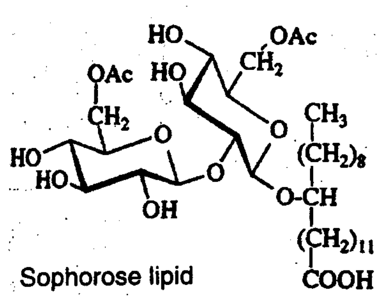
당함유 생계면활성제

Lhamno lipid





Trehalose ester



Sophorose lipid

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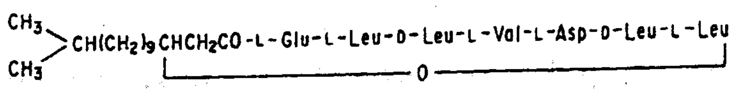
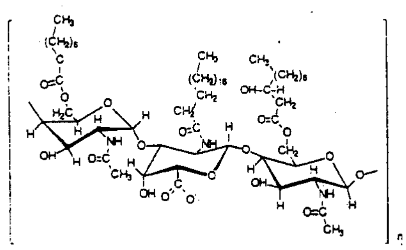
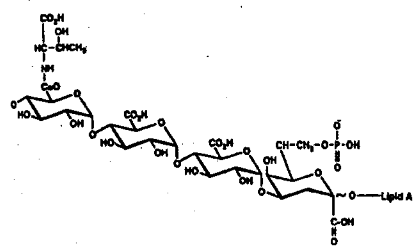
기 타

Surfactin





Emulsan



Lipopoly
saccaride

생체 계면활성제의 응용

생계면활성제의 응용분야

응용분야	기능	생계면활성제
Fine chemicals	Emulsifying, spreading agents Wetting, penetrating agents Special pigments Antistatic agents Polymer materials	Trehalose lipid Corynomycolic acid Spiculisporic acid
Pharmaceuticals	Immune activation Thrombus solubilization Gall stone solubilization Antibiotics Drug carrier	Code factor Surfactin Bile acids Sophorolipids Rhamnolipids
Agriculture	Pestisides	Lecithin
Biochemicals	Protein solubilizers Liposome materials	Sucrose lipids Phospholipids
Cosmetics	Skin moisturizers Skin care Sweat control	Sophorolipids Emulsan Agaricic acids
Food additives	Foaming agents Emulsifying agents Stabilizers (bakery)	Saponin Lecithin Mannosylerythritol lipids

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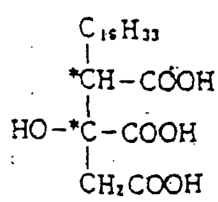
Biosurfactants for detergents?

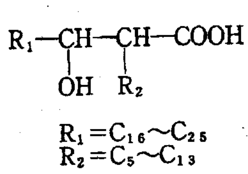
생체 계면활성제의 응용

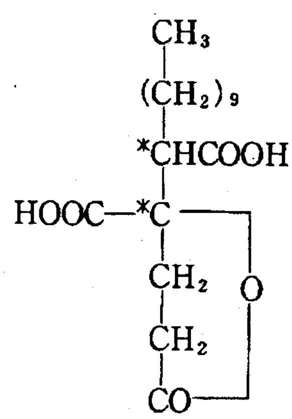
지방산계 생계면활성제

Agaricic acid



Corynomycolic aicd





Spiculiosporic acid

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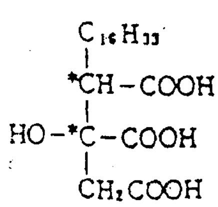
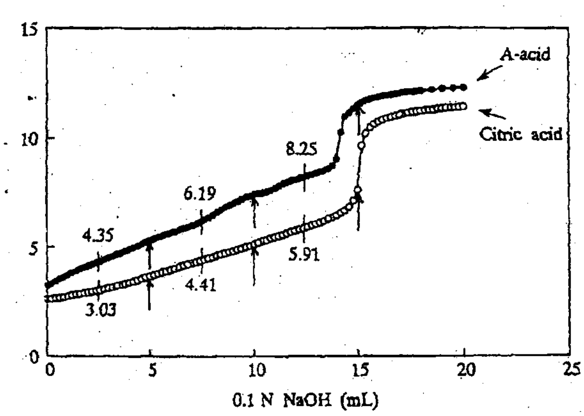
생계면활성제의 제조수율예

원료명	화 합 물	균주 origin	Microorganism	생산량(g/L)
당지질계	Trehalolipid	Bacteria	*Arithobactor*	1.3
	Rhamnolipid	Bacteria	*Pseudomonas*	3.4 (A 형) 10.2 (B 형)
	Sopholipid	Yeast		120
	Mannosylerythrolipid	Yeast		36
	올리고당지방에스터		*Candida* sp	22.5
지방산계	Corynomycolic acid	Bacteria	*Corynebacterium*	2~3
	Spiculisperic acid	Bacteria	*Penicillin*	110
리포 아미노산	Surfactin		*Bacillus*	0.050

생체 계면활성제의 응용

Agaricic acid의 ionization





The pH titration curves of agaricic acid and citric acid at 25℃.

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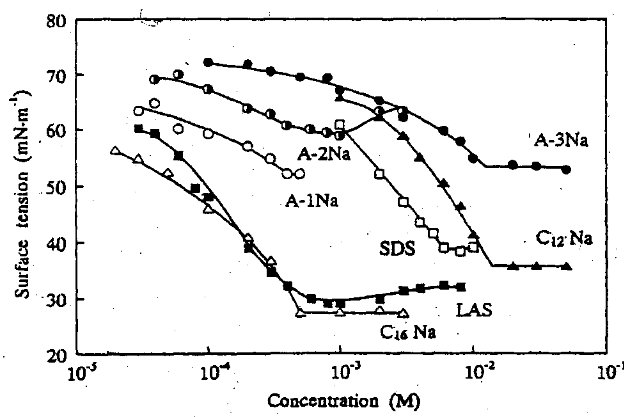
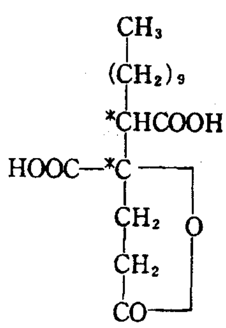
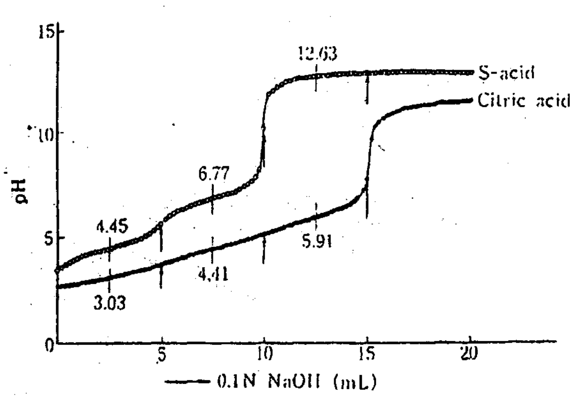
A. acid vs. other detergents



Surface tension *vs* concentration curves of various detergents at 25℃.

S. acid의 ionization





The arrow points show the end points.

The pH titration curves of S-acid and citric acid at 25℃.

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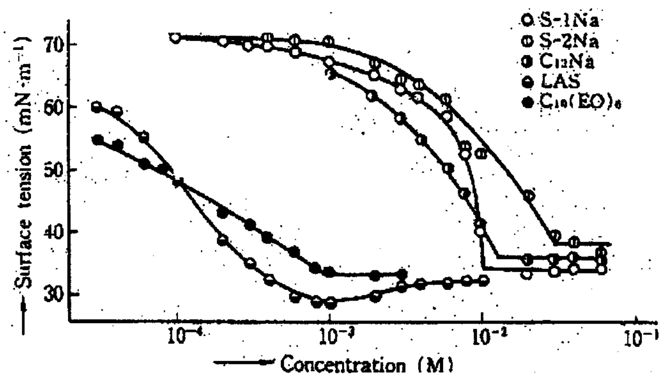
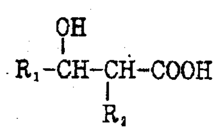
S. acid vs. other detergents



Surface tension *vs.* concentration curves of various detergents at 25℃.

생체 계면활성제의 응용

Natural Corynomycolic Acid



Microorganism	Alkyl chain length		Yield (g/L culture broth)
	R_1	R_2	
Arthrobacter paraffineus	18~23	7~12	0.6
Corynebacterium lepus	16~25	6~14	0.2
Rhodococcus erythropolis	16~25	8~13	0.2

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Biosurfactant Containing Corynomycolate

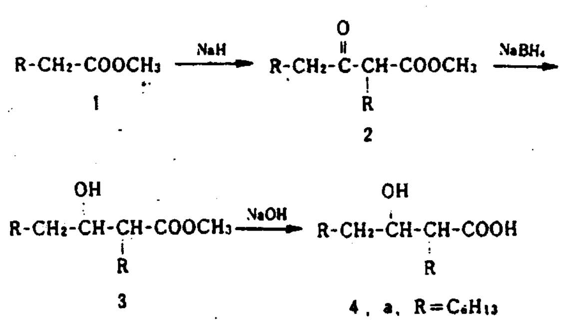
Surface active properties of glycolipids from Arthrobacter sp. in synthetic deposit water at 40 °C.

Surfactant	Minimum surface tension (mN/m)	CMC (mg/L)	Minimum Interfacial Tension (mN/m)	CMC (mg/L)
Mannose-6-corynomycolate	40	5	19	50
Glucose-6-corynomycolate	40	10	9	20
Maltose-6-corynomycolate	33	1	1	20
Maltose-6, 6'-dicorynomycolate	46	10	13	10
Cellobiose-6-corynomycolate	35	3	1	4
Maltotriose-6,6',6''-tricorynomycolate	44	20	19	10

* Interfacial tensions were measured against n-hexadecane.

생체 계면활성제의 응용

The Synthesis of Corvnomvcolic acid



4, a. $R=C_6H_{13}$
b. $R=C_{10}H_{21}$

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The Physical Properties of Corynomycolic acid

Table-2 Surface active properties of synthetic corynomycolic acids and the related biosurfactants.

Biosurfactant *etc.*		cmc (M)	γ_{cmc} (mN/m)	Interfacial tension (mN/m)	Emulsifying action*1 (%)
Synthetic Corynomycolic acid	4 a-Na	8.0×10^{-2} (30℃)	30.0 (30℃)	1.2 (25℃, 0.05% soln./kerosene)	89 (0.5%/kerosene)
	4 b-Na	2.6×10^{-3} (30℃)	28.3 (30℃)	-	100 (0.5%/kerosene)
Natural corynomycolic acid[1)]		*ca.* 5.6×10^{-4} (20℃)	40 (20℃)	10 (20℃, 0.05% soln./hexadecane)	-
Fatty acid soaps	Na laurate*2	2.6×10^{-2} (25℃)			-
	Na stearate[1)]		68 at 0.05%	34(20℃, 0.05% soln. /hexadecane)	-
	Na 2-hydroxy stearate[1)]		47 at 0.05%	10(20℃, 0.05% soln. /hexadecane)	-

*1 Emulsifying action of 0.5% SDS : 66% ; 0.5% NP-9 : 87%.
*2 K. Takahashi ed. (Nippon Fats and Oils Co.), "Kaimen Kasseizai Handbook", Kogaku Tosho Co. (1968), p. 109.

Penetrating action of CM

Penetrating agents	Concn. (%)	Sinking time (s) Cotton	Sinking time (s) Felt
4 a-Na	0.1	>500	>500
〃	0.5	>500	0.8
〃	1.0	0.1	0.1
4 b-Na	0.5	>500	>500
A. OT	0.1	1.2	0.8

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Dispersing properties of CM

Dispersing actions for α−copper phthalocyanine blue (α−Pc).

Dispersants	Concn. (%)	Dispersing action (by turbidity)
4 a−Na	0.1	51
〃	0.5	80
4 b−Na	0.1	27
〃	0.5	75
Rhammolipid A	0.1	44
〃 B	0.1	75
NaSTL	0.1	37
A・OT	0.1	46
NP−11	0.1	71

Fluidity of the membrane

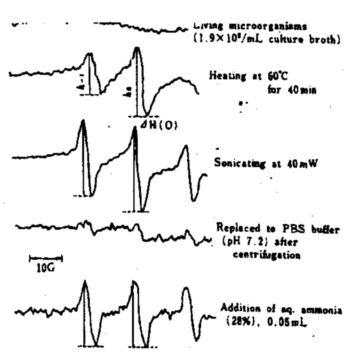

Fig.−1 Changes in ESR spectra of *Candida bombicola* ATCC 22214 depending on the treatment for the microorganism by means of ESR using 16−doxyl−stearic acid as the spin probe at 25℃.

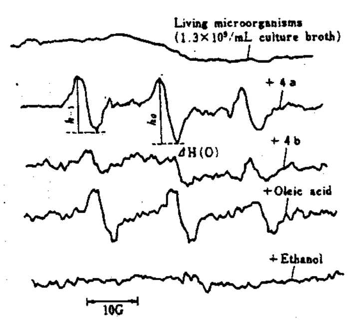

Fig.−2 Effect of synthetic corynomycolic acids on the membrane fluidity of *Candida bombicola* ATCC 22214 by means of ESR using 16−doxyl−stearic acid as the spin probe at 25℃.

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Fluidity of the membrane

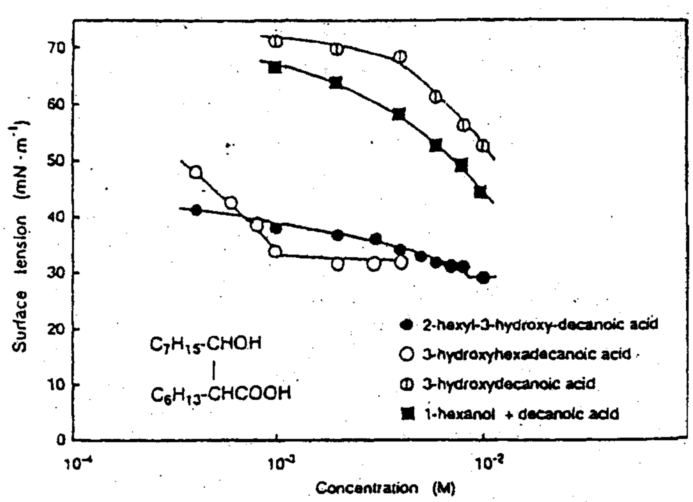
Adding effect of corynomycolic acids on the living cells of *Candida bombicola* ATCC 22214 (glucose grown).

External additive	τ_2 (s)
Culture broth only(pH 7.1)	$>10^{-7}$
4 a*	2.0×10^{-10}
4 a-Na*	$<10^{-12}$
4 b*	5.0×10^{-10}
4 b-Na*	$<10^{-12}$
Oleic acid*	1.2×10^{-10}
Sodium oleate*	1.8×10^{-10}
SDS*	2.0×10^{-10}
Ethanol, 3 μL	$>10^{-7}$

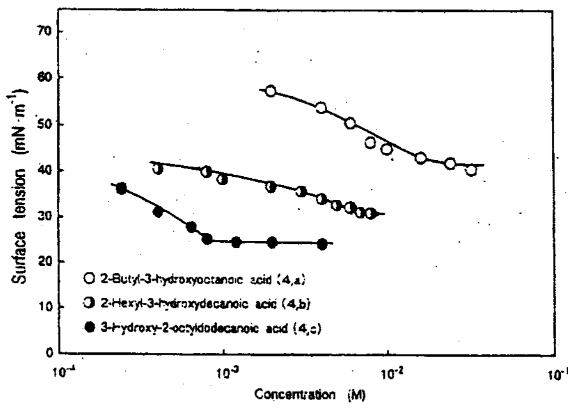
*1.0 mg was added to 1 mL of the culture broth.

생체 계면활성제의 응용

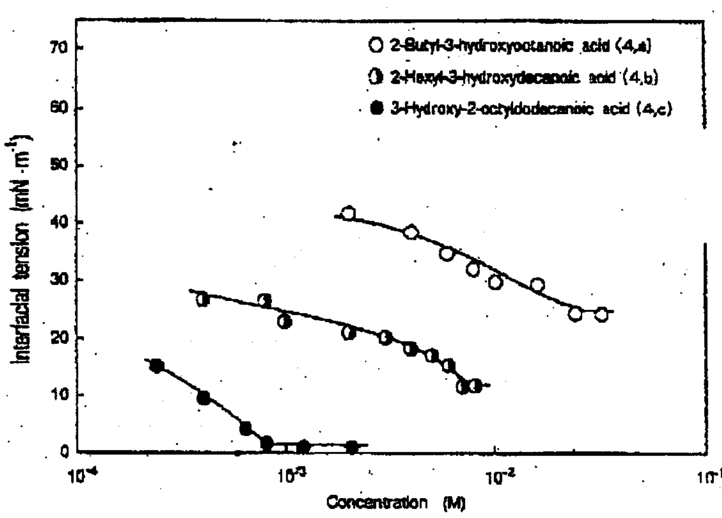
Surface tension vs. concentration



Surface tension vs. concentration



Interfacial tension vs. concentration



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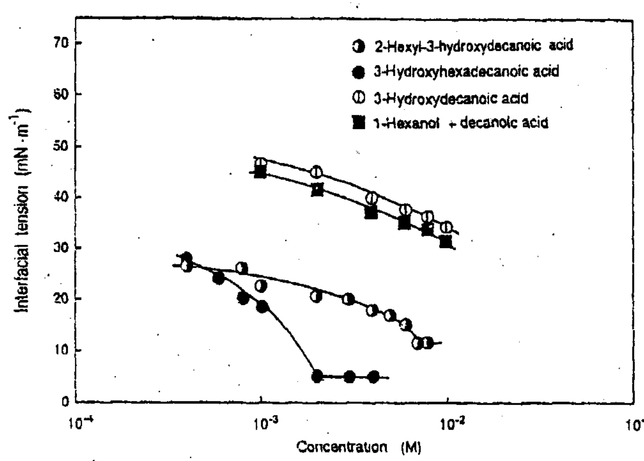
Interfacial tension vs. concentration



생체 계면활성제의 응용

pH vs. Surface activity

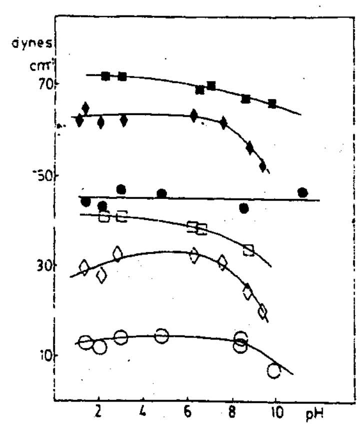


FIG. 5. Data for saturated solutions (0.5 mg/ml) of three carboxylic acids vs pH: octadecanoic acid, surface tension (■) and interfacial tension (□); 12-hydroxy-octadecanoic acid, surface tension (●) and interfacial tension (○); and 2-hydroxy-octadecanoic acid, surface tension (◆) and interfacial tension (◇).

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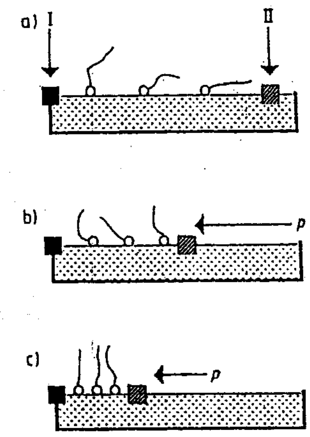
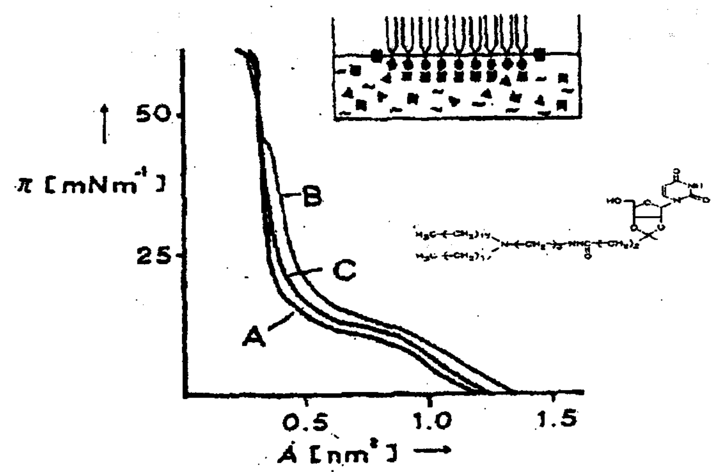


Fig. 5. Operation of a film balance with which, by means of a mobile barrier, it is possible to mechanically reorient molecules in the monolayer system. I = fixed barrier; p = pressure on the mobile barrier II. a) "Gaseous" phase; b) "liquid-expanded" phase; c) "condensed" phase.

생체 계면활성제의 응용



Isotherms of the uridine lipid 62 on different subphases (20°C) [169b]: A) water; B) 0.01 M adenine (complementary) (■); C) 0.01 M thymine (noncomplementary) (▲). π = surface pressure, A = area per molecule.

Pressure-area isotherms of synthetic corynomycolic acid

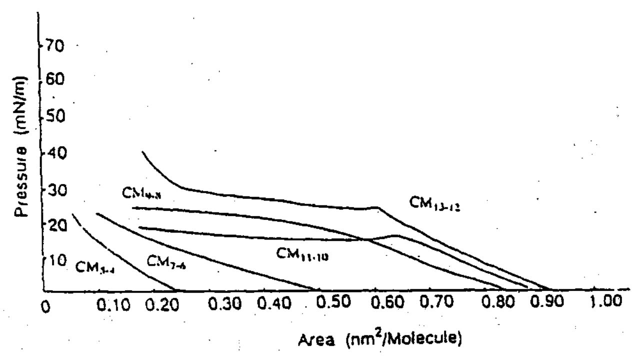
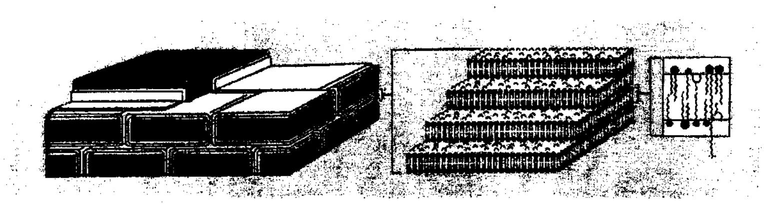


Fig.-2 Pressure-area isotherms of synthetic corynomycolic acids at 25°C.

New concept for the barrier function of the skin



The schematic representation of stratum corneum: "the brick and mortar model"

"The lamellar lipid layers represent the barrier of the skin"
Arch. Dermatol. Res., 282, 45 (1989), J. Dermatol., 112, 1 (1985)
"특별한 피지성분이 피부의 보습성 혹은 보호기능을 부여하는 것은 아니고 피지의 라멜라 gel 구조 그 자체가 이들 기능을 실현하고 있는 것이다."
Fragrance J., 27 (6), 85 (1999)

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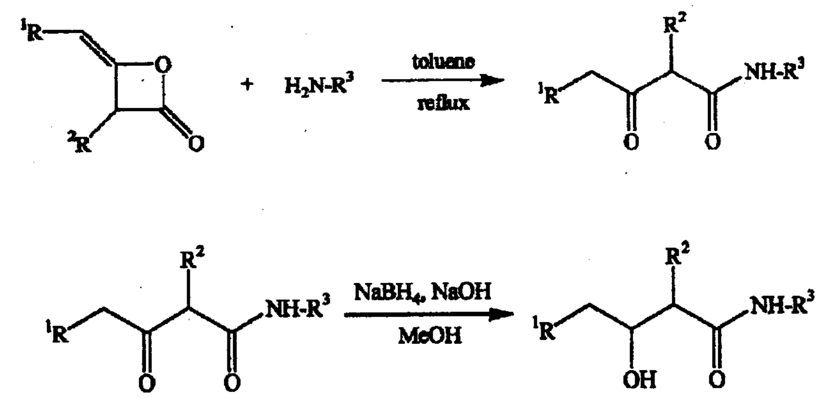
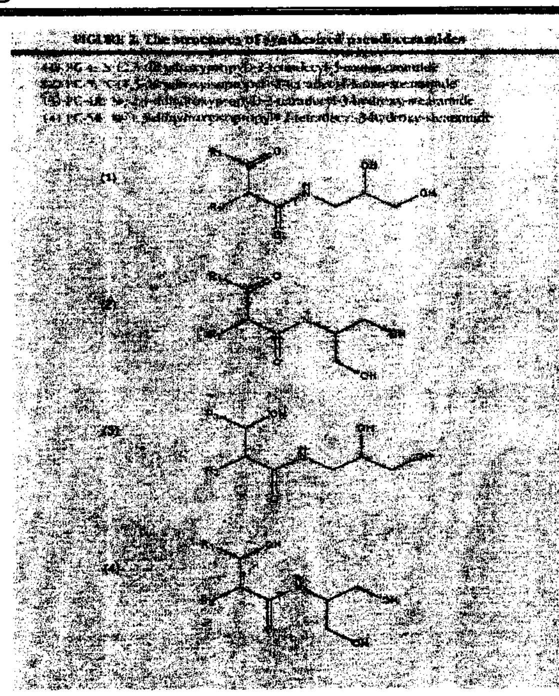
Pseudo-ceramide containing corynomycolic acid backbone





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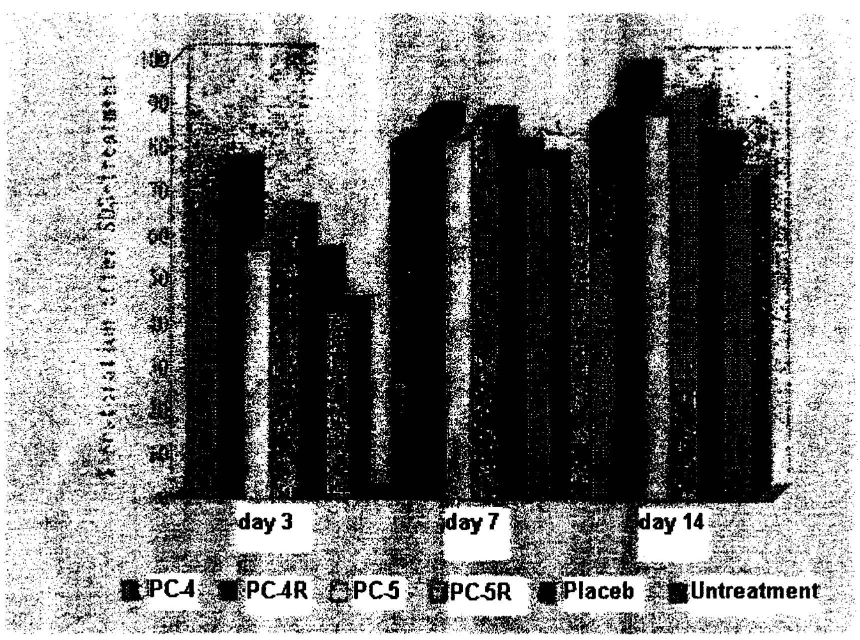
Cross-polarized microscopic picture of multi-lamella emulsion containing PC-4

생체 계면활성제의 응용



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Biosurfactants

	Product	Organization	Productivity	Remarks
Glycolipid	Sophorolipid	Kao	120g/L	Humectant (SOFINA)
	Mannosyl erythritol lipid	Tsukuba Univ.	35.4g/L (as lipid) 25.4g/L (as n-alkane)	
	Rhamnolipid	Tokyo Univ.	2.5g/L	
	Trehalose	Kyowa Hakko	1.3g/L	Difficult to modify because of ester bond
Lipo-amino acid	Cerilin	Shizouka Univ.		
	Emulsifying Factor	Asahi Kasei		Suitable for emulsifying hydrocarbon
Fatty acid	Spiculisporic	Tsukuba Univ.	110g/L	Low foaming activity antielectrostatic agent
Sugar ester		Kyowa Hakko	1.5g/30g cell	Bioconversion from fructose and lauric acid
Sugar ester		Kitasato Univ.		Bioconversion using lipase recovery 88%
N-Acyl amino acid		Ajinomoto	1.7mg/0.47g cell	Bioconversion from glutamic acid and fatty acid
Phosphatidyl glycerol		Yakult		From soybean lecithin using phospholipase D
Lysolecithin		Kyowa Hakko		
Oligosaccharide fatty acid ester		Nihon Surfactant	22.5g/L	

Biosurfactants

기술개발에 대한 요구:

1) 생체시스템과의 친화성
2) Safety
3) 환경오염방지 및 응용기술소재

해결하여야 할 문제:

1) 경제성 확보(생산 수율의 증대)
2) 고부가가치 응용분야의 창출

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