Reaction of Excess Quinoline 1-Oxide with Diketene in Acetic Acid——To a solution of 4.35 g (0.03 mole) of quinoline 1-oxide in 50 ml of AcOH was added 0.84 g (0.01 mole) of diketene dropwise at 15—20° with stirring. After allowing to stand at room temperature for 12 hr, the mixture was condensed under reduced pressure. The residue was taken up in 10% HCl. The HCl solution was made alkaline with K_2CO_3, and extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated to dryness to give a residue. The residue was chromatographed over alumina using ether as a solvent to give a small amount of orange prism of mp 76—78°, undepressed with an authentic sample[7] of 2-acetonylquinoline (VII) prepared according to the literature. From the ether eluent, 2.35 g (54%) of quinoline 1-oxide were recovered.

Reaction of 2-Acetonylquinoline (VII) with Diketene——To a solution of 1.85 g of VII in 10 ml of AcOH was added 2.0 g of diketene dropwise. After stirring for 2 hr at 50°, the reaction mixture was condensed under reduced pressure. The resulting residue was purified by recrystallization from ether to give colorless needles of mp 124—125°, undepressed on admixture with a sample of I. Yield, 1.97 g (78.5%).

7) T. Okamoto and H. Takayama, *Chem. Pharm. Bull.* (Tokyo), **11**, 514 (1963).

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Constituents of Asclepiadaceae Plants. XXXI.[1] Component of *Stapelia grandiflora* Mass

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We have studied the components of *Stapelia grandiflora* Mass from Pakistan and isolation of the components was carried out as indicated in Charts 1 to 3.

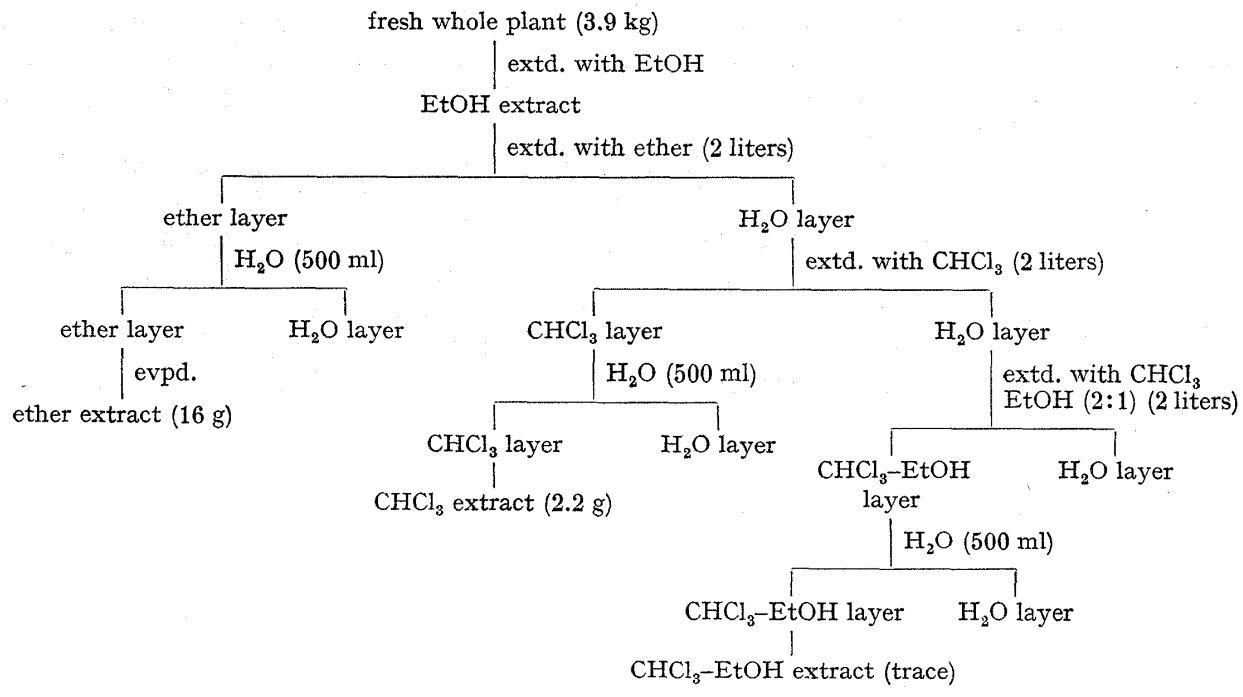

Chart 1

1) Part XXX: H. Mitsuhashi and K. Tomimoto, *Syôyakugaku Zasshi*, **25**, 7 (1971).
2) Location: *a) Research Laboratories, Daiichi Seiyaku Co., Ltd., Minamifunabori-cho, Edogawa-ku, Tokyo, 132, Japan; b) Kita-12-jo, Nishi-5-chome, Kita-ku, Sapporo, 060, Japan.*

dried whole plant (280 g)
extd. with $CHCl_3$
precipitate | $CHCl_3$ extract (35.1 g)
extd. with MeOH (4 liters)
MeOH extract (31 g)

Chart 2

fresh whole plant (2.5 kg)
extd. with MeOH (7 liters)
MeOH extract (110 g)
extd. with hexane (1 liter)
soluble fraction (17 g) | insoluble fraction (64 g)

Chart 3

Chloroform extract in Chart 1, MeOH extract in Chart 2, and hexane-insoluble fraction in Chart 3 were found to be a mixture of crude glycosides. Each extract was hydrolyzed with H_2SO_4 to give crude ester-type aglycones, which gave the same chromatogram on thin-layer chromatography (TLC), and the mixture of aglycones obtained from the extracts were combined and subjected to column chromatography and preparative TLC to give an amorphous aglycone showing one spot on TLC (ester-1) (I). The ultraviolet (UV) absorption spectrum of the ester-I (I) showed maximum at 216.5 nm (ε=8500). The infrared (IR) spectrum displayed absorptions due to hydroxyl groups at 3620 cm^{-1}, 3380 and conjugated ester group at 1700, 1645, and 1270—1200 cm^{-1}.

The mass spectrum showed *m/e*: 432 (M^+), 414 (M^+-H_2O), 396 (M^+-$2H_2O$), 332 (M^+-100), 314 (M^+-100-H_2O), 296 (M^+-100-$2H_2O$), 138 (ion peak due to retro-Diels-Alder fragmentation), 120, and *m/e*: 83 as a base peak. The nuclear magnetic resonance (NMR) spectrum showed a singlet at δ: 1.00 ppm (18-CH_3), a singlet at 1.27 (19-CH_3), a doublet at 1.24 (J=6.0 Hz 21-CH_3), a multiplet at 1.77—1.88 (vinylic methyl), at 3.11 (OH), integrating three protons which disappeared on addition of D_2O, a multiplet at 3.48 assigned to $C_{3\alpha}$-H geminal to a hydroxyl group, a quartet 3.81 (J=6.0 Hz, C_{20}-H), a multiplet at 4.57 (methyne proton), a multiplet at 5.38 (C_6-H), a quartet at 6.10 (J=8.0 Hz, vinyl proton), integrating one-half proton and a quartet at 6.89 (J=6.0 Hz, vinyl proton) similar to one-half proton.

The deacylaglycone (II) obtained from alkaline hydrolysis of the ester-I (I) gave a molecular ion peak at *m/e*: 350 in the mass spectrum, since the molecular peak of the ester was *m/e*: 432, the ester-I (I) had a fatty acid with a molecular weight 100. The acidic portion was the mixture of geometric isomers and suspected to be angelic- and tiglic- acid by NMR, and gas liquid chromatography.

The deacylaglycone (II) showed a singlet at δ: 1.04 ppm (18-CH_3), a singlet at 1.08 (19-CH_3), a doublet at 1.19 (J=6.0 Hz, 21-CH_3), a multiplet at 3.17—3.50 integrating two protons (methyne proton attached to a hydroxyl group), a triplet at 3.76 integrating one proton (methyne proton attached to a hydroxyl group), a multiplet at 5.39 (C_6-H). Since the signal of δ: 3.76 ppm was assigned to 12α-H,[3] the deacylaglycone (II) was presumed to be boucerin. As a result of comparison with authentic boucerin, which was isolated from *Boucerosia aucheriana* Decne (Asclepiadaceae) by Mitsuhashi, *et al.*,[4] the *Rf* value on TLC, coloration by $SbCl_3$, and fragmentation in the mass spectrum of the deacyl-agly-

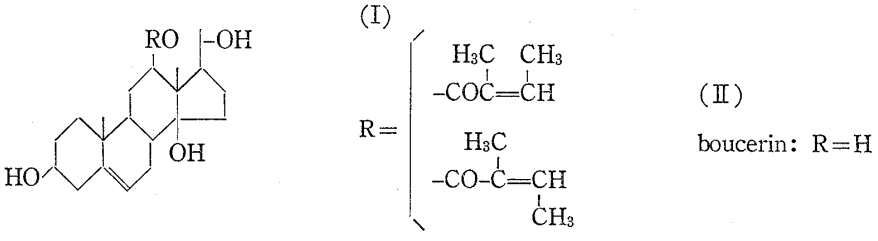

Fig. 1

3) Y. Shimizu and H. Mitsuhashi, *Tetrahedron*, **24**, 4143 (1968).
4) H. Nikaido, Y. Shimizu, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **15**, 725 (1967).

cone (II) were identical with those of boucerin. In addition, there was no depression of mp in mixed melting point test, and deacylaglycone (II) was identified as boucerin. The ester (I) was presumed to be a mixture which was constituted of tiglic acid ester and angelic acid ester of (II) from the consideration of vinyl–methyl group and vinyl proton in the NMR spectrum of the ester (I).[5] However, the ester (I) has not been separated into tigloylboucerin and angeloylboucerin, up to now. The NMR signal due to a proton on $C_{12\alpha}$ of boucerin (II) appears at δ: 3.76 as triplet, the same proton of compound I shifted to δ: 4.57. By the comparison of chemical shifts and the coupling constants with polyoxypregnane ester compounds,[6,7] the ester linkage is located at 12β-hydroxyl group of boucerin (II).

Experimental

Melting points were measured on a Kofler hot stage and are not corrected. NMR spectra were recorded on a JOELCO-PS-100 with tetramethylsilane (TMS) as internal standard and abbreviation used are s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet. TLC was performed on silica gel (Kiesel gel HF_{254}, Merck). Column chromatography was run on silica gel (0.05—0.2 mm, Merck).

Extraction and Isolation——Extraction and isolation procedures are shown in Charts 1, 2, and 3. Each fraction was checked by TLC.

Hydrolysis of the Glycoside——A solution of 2.2 g of the crude glycosides from the $CHCl_3$ extract dissolved in 80 ml of MeOH was refluxed for 1 hr with 80 ml of 0.1N H_2SO_4 on a water bath, 80 ml of H_2O was added, MeOH was evaporated *in vacuo*, and the residual aqueous solution was heated at 60° for 20 min. The resulting mixture was extracted five times with 50 ml of $CHCl_3$, which was washed with 5% $NaHCO_3$ solution and H_2O, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave 1.0 g of a crude ester-type aglycone. Similar as above, the crude glycoside from MeOH extract gave 7.0 g of a crude ester-type aglycone and that from hexane-insoluble fraction gave 5.0 g.

Ester-I——From 13 g of a crude ester-type aglycone, 103 mg of ester-I was obtained by column chromatography and preparative TLC. UV λ_{max}^{EtOH} nm (ε): 216.5 (8500). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620, 3380, 1700, 1645, 1270—1200. NMR (δ) $CDCl_3$: 1.00 (s, 3H), 1.27 (s, 3H), 1.24 (d, J=6.0 Hz, 3H), 3.11 (m, 3H), 3.48 (m, 1H), 3.81 (q, J=6.0 Hz, 1H), 4.57 (m, 1H), 5.38 (m, 1H), 6.10 (q, J=8.0 Hz, 1/2 H), 6.89 (q, J=6.0 Hz, 1/2 H).

Boucerin——Ester-I dissolved in 3 ml of 5% KOH–MeOH solution was refluxed under N_2 gas for 5.5 hr, 1 ml of H_2O was added, and MeOH was evaporated *in vacuo*. The resulting mixture was poured into 7 ml of H_2O and extracted three times with 20 ml each of $CHCl_3$–EtOH (2: 1) solution. The solvent was evaporated and the residue was purified by preparative TLC to give 22 mg of prisms from $Me_2CO/CHCl_3$, mp 231—236°; Pb $(OAc)_4$ test, negative. NMR (δ) CD_3OD: 1.04 (s, 3H), 1.08 (s, 3H), 1.19 (d, J=6.0 Hz, 3H), 3.76 (t, J=7.0 Hz, 1H), 5.39 (m, 1H). Mixed fusion with authentic boucerin (mp 231—240°) from *Boucerosia aucheriana* showed no depression.

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5) J. Niwa and H. Kasiwagi, *Bull. Chem. Soc. Japan*, **36**, 1414 (1963).
6) T. Yamagishi and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **20**, 625 (1972).
7) T. Sasaki, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **20**, 628 (1972).