steric hindrance. For the reason why the reaction constants (ρ) of Fig. 1 and Fig. 2 are not equal, we presume the influence of electric field that is possessed by *ortho*-substituted benzoic acids.

Pyridine used for this experiments had moisture content of 10^{-4} mole fraction or below, which were checked by measuring the shift of two component system of pyridine-acetic acid.[9] When pyridine contains more moisture, the larger marginal difference in δ_0 value will be resulted. Therefore, we had employed an experimental apparatus to prevent a moisture contamination while sampling; all experiments were conducted under high vacuum of $10^{-5.3}$ through $10^{-4.7}$ mm. Hg and satisfactory results were obtained in good reproducibility.

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Glycosides from the Leaves of *Euptelea polyandra* SIEB. et ZUCC.[*1,*2]

In the course of our investigations[*3,1] on anti-microbial substances in buds or young leaves with more than one thousand species of plants, the authors found that the juice of the leaves of *Euptelea polyandra* SIEB. et ZUCC. (Eupteleaceae) showed strong activities against some phytopathogenic fungi. Two active principles were isolated and named eupteleoside A and eupteleoside B respectively, and their chemical structures investigated.

Eupteleoside A (I), colorless needles, m.p. 269~271°, $[\alpha]_D^{22}$ +5.5° (c=1.1, pyridine), IR ν_{max}^{KBr} cm^{-1}: 3500 (OH), 1768 (lactone), (*Anal.* Calcd. for $C_{46}H_{70}O_{17}\cdot 2H_2O$: C, 59.33; H, 8.01. Found : C, 59.42; H, 7.70), is positive in the Liebermann-Burchard reaction (reddish purple), but gives negative coloration with tetranitromethane or with ferric chloride. I, on acetylation with acetic anhydride and pyridine gives eupteleoside A octaacetate (II), m.p. 179~181°, $[\alpha]_D^{22}$ +25° (c=1.10, chloroform), (*Anal.* Calcd. for $C_{62}H_{86}O_{25}\cdot H_2O$: C, 59.60; H, 7.10; $8CH_3CO$, 27.56. Found : C, 59.69; H, 7.08; CH_3CO, 27.54), and on methylation,[2]

[*1] This paper forms part of the series by Sueo Tatsuoka "Studies on the Useful Components in Natural Sources."

[*2] Papers partly presented at the 83rd Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, November, 1963.

[*3] Partly presented at the Annual Meeting of the Pharmacognostical Society of Japan, Chiba, July, 1963.

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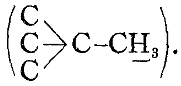
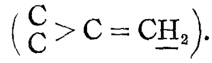
affords eupteleoside A octa-O-methyl ether (III), m.p. 198°, $[\alpha]^{22}_{D}$ +25° (c=0.88, chloroform), *Anal.* Calcd. for $C_{54}H_{86}O_{17}$: C, 64.39; H, 8.60; $8CH_3O$, 24.64. Found : C, 64.40; H, 8.60; CH_3O, 24.03), which shows no hydroxyl band in its infrared spectrum.

Acid hydrolysis of I gives eupteleogenin (IV) and one mole each of L-rhamnose, L-arabinose and D-glucose, the sugars being separated by chromatography on powdered cellulose with butanol saturated with water, and identified as their phenylosazones.

Eupteleogenin (IV), colorless needles, m.p. 268~272°, $[\alpha]^{22}_{D}$ +83° (c=0.53, chloroform), (*Anal.* Calcd. for $C_{29}H_{42}O_4$: C, 76.61; H, 9.31. Found : C, 76.70; H, 9.19), shows the correct analysis for the formula $C_{29}H_{42}O_4$. The presence of one hydroxyl group, a five membered lactone moiety and one vinyl type of double bond in eupteleogenin was demonstrated by the following reactions : Acetylation of IV with acetic anhydride and pyridine gives eupteleogenin acetate (V), m.p. 321~322°, $[\alpha]^{22}_{D}$ +87° (c=0.60, chloroform), (*Anal.* Calcd. for $C_{31}H_{44}O_5$: C, 74.96; H, 8.93. Found : C, 74.99; H, 8.74). Oxidation of IV with chromium trioxide affords eupteleogenone (VI), m.p. 242°, $[\alpha]^{21}_{D}$ +78° (c=0.60, chloroform), (*Anal.* Calcd. for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found : C, 77.13; H, 8.99).

The strong absorption band at 1766~1768 cm^{-1} in the infrared spectra of compounds (IV, V and VI), and relatively intense peaks at m/e 426 (M−28 (CO)[3]) and 410 (M−44 (CO_2[4])) in the mass spectrum[*4] of IV, strongly suggest the presence of a five membered lactone ring. IV was hydrolysed with potassium hydroxide in methanol and the resulting acid was treated with diazomethane to give the methyl ester (VII), m.p. 175°, IR $\nu^{\mathrm{Nujol}}_{\mathrm{max}}$ cm^{-1}: 1728 (ester CO), (*Anal.* Calcd. for $C_{30}H_{46}O_5 \cdot \frac{1}{2}H_2O$: C, 72.68; H, 9.55. Found : C, 72.52; H, 9.57). Acetylation of VII gives the diacetate (VIII), m.p. 113~114°, IR $\nu^{\mathrm{Nujol}}_{\mathrm{max}}$ cm^{-1} : 1725 (ester); 1735 (acetyl), (*Anal.* Calcd. for $C_{34}H_{50}O_7$: C, 71.54; H, 8.83. Found : C, 71.23; H, 8.83), which shows no hydroxyl absorption band in its infrared spectrum (CCl_4). The nature of the fourth oxygen in the aglycone is now being investigated.

Eupteleogenin (IV) reveals five three-proton singlets (total 15H) at 0.80 (3H), 0.99 (3H), 1.03 (3H), 1.06 (3H) and 1.14 (3H), and a signal (2H, broad) at 4.73 p.p.m. (δ) in its nuclear magnetic resonance spectrum,[*5] while the acetate (V) exhibits singlets at 0.85 (6H), 1.05 (6H), 1.13 (3H) and at 4.73 (2H) p.p.m. (broad). The fifteen protons in the region of 0.80 to 1.14 p.p.m. can therefore be accounted for five C-methyls  $\left(\begin{matrix}C\\C\\C\end{matrix}\!\!>\!C-C\underline{H}_3\right)$. The two protons at 4.73 p.p.m. are assigned to an exomethylene group  $\left(\begin{matrix}C\\C\end{matrix}\!>\!C=C\underline{H}_2\right)$. The above assumption receives further support by the catalytic hydrogenation of IV to yield dihydroeupteleogenin (IX), m.p. 294~296° (*Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.27; H, 9.71. Found: C, 76.22; H, 9.88), the nuclear magnetic resonance spectrum of which lacks the peak at 4.73 p.p.m., and adds a newly formed C-methyl signal (one peak of the doublet at 0.93 p.p.m.). In addition to this, the ozonolysis of IV gave formaldehyde and a saturated ketone (X), m.p. 298~300°, IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1} : 1775 (lactone), 1708 (6-membered ring ketone), (*Anal.* Calcd. for $C_{28}H_{40}O_5$: C, 73.65; H, 8.83. Found : C, 74.00; H, 8.78).

Further studies of these and related compounds as well as their biological properties are under investigations and will be reported elsewhere.

[*4] The mass spectrum was measured at the Laboratory for Mass Spectrometry, Karolinska Institute, Stockholm, Sweden, by the courtesy of Prof. S. Shibata.

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Studies on the Optical Rotatory Dispersion of Carbohydrate C-Nitroalcohols

As in the case of stereochemistry of carbonyl compounds, usefulness of optical rotatory dispersion (ORD) has been recognized in the field of carbohydrate chemistry[1~3] and also in the stereochemistry of some kinds of nitro compounds, such as nitro steroids.[4] However, no report has been published on ORD curves of carbohydrate C-nitroalcohols.[*1]

In the present communication, the writers wish to report on ORD curves of some epimeric pairs of carbohydrate C-nitroalcohols such as 1-nitro- and 1-nitro-2-acetamido-polyhydroxyalkanes, which were obtained as intermediates in the process of carbohydrate synthesis by the Sowden's nitromethane method.[5~7] In addition the writers wish to discuss on the relationship between the sign of an ORD curve and chemical structure.

All compounds examined showed a shoulder at 270~280 mμ in their ultraviolet absorption spectra due to nitro chromophores, and, as shown in Table I, these compounds gave positive or negative Cotton effect curves with the first extrema at 330~340 mμ; 1-nitro-1-deoxy-D-mannitol (I),[8] 1-nitro-1-deoxy-D-glycero-D-talo-heptitol (II),[9] 1-nitro-1-deoxy-D-glycero-L-gluco-heptitol (III),[10] 1-nitro-2-acetamido-1,2-dideoxy-D-mannitol (IV)[6] and 1-nitro-2-acetamido-1,2-dideoxy-D-glycero-D-talo(?)-heptitol (V)[11] exhibited negative Cotton effects, while 1-nitro-1-deoxy-D-glucitol (VI),[8] 1-nitro-1-deoxy-D-glycero-D-galacto-heptitol (VII),[9] 1-nitro-1-deoxy-D-glycero-L-manno-heptitol (VIII),[10] 1-nitro-2-acetamido-1,2-dideoxy-D-glucitol (IX)[6] and 1-nitro-2-acetamido-1,2-dideoxy-D-glycero-D-galacto(?)-heptitol (X)[11] showed positive Cotton effects.

[*1] At the 83rd Annual Meeting of Pharmaceutical Society of Japan on November 1, 1963, one (Satoh) of the present writers reported that 1-nitro-2-acetamido-1,2-dideoxy-D-mannitol and corresponding D-glucitol showed a negative, and a positive Cotton effect, respectively, and the data are to be published in this Bulletin.

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