1667 (carbonyls). A mono-N-methyl compound (**6**), mp 308—310°, UV λ_{max}^{EtOH} nm (log ε): 242.5 (4.62) and 273 (4.26), IR ν_{max}^{KBr} cm^{-1}: 3450 (NH), 1715, 1685 and 1660 (carbonyls), was isolable. Methylation of **1** with methyl iodide–K_2CO_3 in DMSO gave a mono-N-methyl derivative **11**, mp 85° in which the pyrrolyl nitrogen had been alkylated; the latter has also been transformed into **6** in the same manner as the sequence **1**→**4**.

6 and **7** upon treatment with trifluoroacetic acid at room temperature yielded **8**, mp 303—306°, IR ν_{max}^{Nujol} cm^{-1}: 3250 (NH), 1720 and 1660 (carbonyls) and **9**, mp 236—238°, UV λ_{max}^{EtOH} nm (log ε): 224 (4.46), IR ν_{max}^{KBr} cm^{-1}: 1700 and 1655 (carbonyls), in good yields. In the NMR spectrum (δ, $CDCl_3$) **9** shows the pyrrole ring proton at 6.19 ppm as a singlet. A Mannich reaction of **9** with dimethylamine and formaldehyde afforded **10**, mp 183—185°.

The results again show the usefulness of our β-aminopyrrole syntheses previously reported.[1]

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Synthetic Study of the Ginseng Sapogenins: Preparation of Dammarenediol-II and Remote Oxidation of Dammaranediols with Photoexcited Nitrobenzene Derivatives

In an attempt toward the syntheses of the Ginseng sapogenins, 20(*S*)-protopanaxadiol-(12β-hydroxydammarenediol-II) (I)[1] and 20(*S*)-protopanaxatriol(6α,12β-dihydroxydammarenediol-II),[2] the synthesis of 3β-acetoxyhexakisnordammaran-20-one (II) has already been reported.[3]

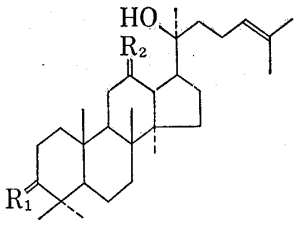
In continuation of this work, dammarenediol-II (III), the constituent of dammar resin was prepared from II. A solution of II and the Grignard reagent prepared from the bromide (IV) in dry ether was refluxed for 4 hr and the reaction product was recrystallized from aqueous MeOH and then nitromethane to give colorless needles, mp 131—132° which was proved to be identical with the authentic sample of III by direct comparison. Although the formation of dammarenediol-I (the C-20 epimer of III) to some extent was expected, its detection in the reaction mixture could not be done as yet because of the difficulty of the separation of III and its C-20 epimer by thin layer chromatography or gas liquid chromatography.

Breslow have recently developed the remote oxidation of the steroids with benzophenone phototriplet succeeding the functionalization of the unactivated carbon atoms of the C and D rings.[4] Since Breslow's procedure involves the dehydration process, it can not be applied to the hydroxylation of the dammarane nucleus owing to the presence of the C-20 tertiary hydroxyl which is difficult to be protected. For the purpose of the introduction of a hydroxyl

1) M. Nagai, T. Ando, N. Tanaka, O. Tanaka, and S. Shibata, *Chem. Pharm. Bull.* (Tokyo), **20**, 1212 (1972) and references cited therein.
2) Y. Nagai, O. Tanaka, and S. Shibata, *Tetrahedron*, **27**, 881 (1971).
3) H. Fujimoto and O. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **18**, 1440 (1970).
4) R. Breslow, *Chem. Soc. Review*, **1**, 553 (1972); R. Breslow, S. Baldwin, T. Flechtner, P. Klicky, S. Lin, and W. Washburn, *J. Am. Chem. Soc.*, **95**, 3251 (1973) and references cited therein.

group at C-12 of the triterpenes of this type, the remote oxidation with the alternative reactant, photoexcited aromatic nitro groups[5] has been explored.

3-Epidammaranediol-II (V), mp 77—78°, was prepared from dipterocarpol (VI) through 3-epidammarenediol-II (VII). A solution of the *p*-nitrophenylacetate (VIII) of V in *tert*-BuOH was irradiated by a high pressure mercury lamp through Pyrex filter under stream



I : R_1=3-OH, 4-H R_2=3-OH, 4-H

III : R_1=3-OH, 4-H R_2=H_2

VI : R_1=O R_2=H_2

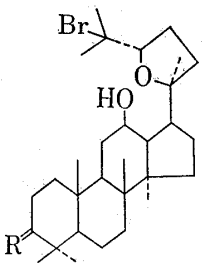
VII : R_1=3-H, 4-OH R_2=H_2

X : R_1=3-H, 4-OH R_2=3-OH, 4-H

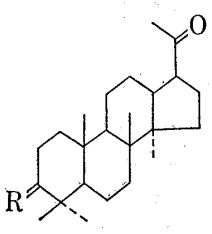
XIII : R_1=3-H, 4-OAc R_2=3-OH, 4-H

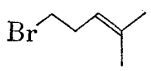
XIV : R_1=3-H, 4-OAc R_2=O

XV : R_1=3-H, 4-OH R_2=3-H, 4-OH

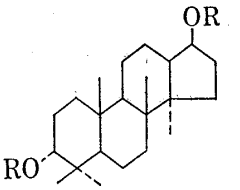


XI : R=3-H, 4-OH XII : R=3-H, 4-OAc

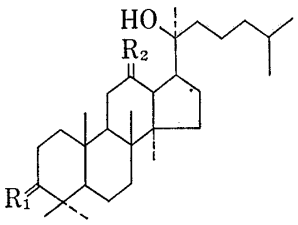




II : R=3-OAc, 4-H XXIV : R=3-H, 4-OAc



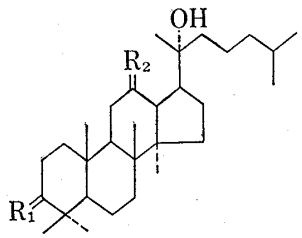
XXI : R=H XXV : R=Ac



V : R_1=3-H, 4-OH R_2=H_2

VIII : R_1=3-H, 4-OOCCH$_2$-(*p*-NO_2-Ph) R_2=H_2

IX : R_1=3-H, 4-OH R_2=3-H, 4-OH



XVI : R_1=3-H, 4-OOCCH$_2$-(*p*-NO_2-Ph) R_2=H_2

XVII : R_1=3-H, 4-OH R_2=H_2

XVIII : R_1=3-H, 4-OH R_2=3-H, 4-OH

XIX : R_1=3-H, 4-OOCCH$_2$CH$_2$-(*p*-NO_2-Ph) R_2=H_2

XX : R_1=3-H, 4-OOC-(*p*-NO_2-Ph) R_2=H_2

XXII : R_1=3-OH, 4-H R_2=H_2

XXVI : R_1=3-H, 4-OAc R_2=H_2

Chart 1

5) Photooxidation of hydrocarbons and saturated alkyl groups with aromatic nitro groups: J.W. Weller and G.A. Hamilton, *Chem. Comm.*, **1970**, 1390; J.A. Barltrop and N.J. Bunce, *J. Chem. Soc. C*, **1968**, 1467; D. Döpp and E. Brugger, *Chem. Ber.*, **106**, 2166 (1973) and references cited therein.

of N_2 for 30 hr. The reaction mixture was saponified with alkali and the product was chromatographed on silica gel to give a triol (IX), mp 157—158°, $[\alpha]_D$ +3° ($CHCl_3$), $C_{30}H_{54}O_3$ in a yield of 13% along with the parent diol (V) (recovery 44%). The nuclear magnetic resonance (NMR) spectrum of IX in $CDCl_3$ exhibited an additional carbinol proton signal at δ 4.30 ppm (1H multiplet $\frac{1}{2}W$=8 Hz) which was similar in the chemical shift as well as the coupling pattern to that due to the 12β-proton of the 12α-hydroxydammarane type triterpene, suggesting the introduction of an axial hydroxyl group at C-12 in this reaction. The confirmation of the structure of IX was established by its preparation from betulafolienetriol (X).[6]

On treatment with NBS in CCl_4, X yielded the bromo-compound (XI).[6] Because the 12β-hydroxyl group of XI was strongly hindered by the cyclized side chain, on the acetylation under the usual condition the selective acetylation of 3α-hydroxyl of XI occurred to give 3-monoacetate (XII) which was reduced with zinc to give 3-O-acetylbetulafolienetriol (XIII), mp 216—218° quantitatively. On oxidation with CrO_3-pyridine, XIII yielded the 12-ketone (XIV), mp 218—220°. The infrared (IR) and NMR spectra were consistent with the assignment of the structures of XIII and XIV, respectively. 12-Epibetulafolienetriol (XV), mp 187—189° prepared from XIV by $LiAlH_4$ reduction was catalytically hydrogenated to afford 12-epibetulafolianetriol, mp 157—158°, which was revealed to be identical with the above triol (IX).

The *p*-nitrophenylacetate (XVI) of 3-epidammaranediol-I (XVII), the C-20 epimer of VII was demonstrated also to yield 12α-hydroxylated compound (XVIII) by the same sequence of the remote oxidation as above in the similar yield. Very recently, Scholl, *et al.* reported the remote oxidation of 5α-androstan-3α-yl β-(*p*-nitrophenyl)propionate.[7] The present authors found that the remote oxidation of the β-(*p*-nitrophenyl)propionate (XIX) of XVII under the same condition also yielded XVIII but the products were rather complicated than the case of *p*-nitrophenylacetate (XVI).

Finally, the remote oxidation of the *p*-nitrobenzoate (XX) of XVII was examined. The irradiation of XX in *tert*-BuOH for 40 hr under the same condition as above followed by alkaline saponification gave a diol (XXI), mp 196—197°, $[\alpha]_D$ +11° (EtOH), $C_{22}H_{38}O_2$ in a yield of 12% along with the parent diol (XVII) (recovery 70%) and its epimerized compound (XXII) (yield 5%). No formation of XVIII was observed in this case and the gas liquid chromatography of the volatile fraction of this reaction mixture indicated the formation of 2-methyl-6-heptanone (XXIII), which was identified as its 2,4-dinitrophenylhydrazone. The structure of XXI, 17-octakisnordammarane-3α,17β-diol was elucidated by the spectral data and by its preparation from XVII *via* XXIV and its Baeyer-Villiger oxidation product (XXV). The irradiation of a solution of the acetate (XXVI) and methyl *p*-nitrobenzoate in *tert*-BuOH afforded only unchanged starting material indicating the intramolecular nature of this novel cleavage reaction. The absence of XXI in the crude reaction products of *p*-nitrophenyl acetates, VIII and XVI, was demonstrated by the thin-layer chromatography. The synthesis of 20(*S*)-protopanaxadiol (I) based on the present results is under progress.

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6) T. Ohsawa, N. Tanaka, O. Tanaka, and S. Shibata, *Chem. Pharm. Bull.* (Tokyo), **20**, 1890 (1972), preliminary communication, *idem*, *Tetrahedron Letters*, **1968**, 4235.
7) P.C. Scholl and M.R. Van De Mark, *J. Org. Chem.*, **38**, 2376 (1973).

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Synthesis of (±)-Methyldecinine

Decinine, a typical Lythraceae alkaloid having a biphenyl linkage, has been isolated from *Decodon verticillatus* (L.) ELL.,[1] *Lagerstroemia indica* L.,[2] and *Lythrum lanceolatum*.[3] Its structure was assigned as shown in I by J.P. Ferris, *et al.*[4] We now report the synthesis of its methyl ether, (±)-methyldecinine (II).

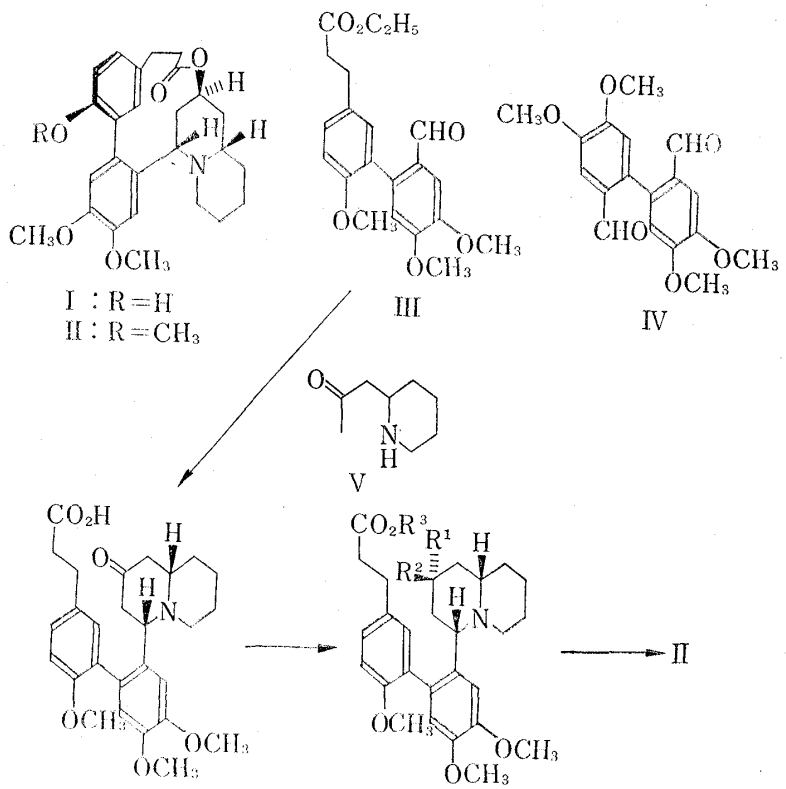

Chart 1

1) J.P. Ferris, *J. Org. Chem.*, 27, 2985 (1962).
2) J.P. Ferris, R.C. Briner and C.B. Boyce, *J. Am. Chem. Soc.*, 93, 2958 (1971).
3) H. Wright, J. Clardy and J.P. Ferris, *J. Am. Chem. Soc.*, 95, 6467 (1973).
4) J.P. Ferris, C.B. Boyce and R.C. Briner, *Tetrahedron Letters*, **1966**, 3641; *idem*, *J. Am. Chem. Soc.*, 93, 2942 (1971).