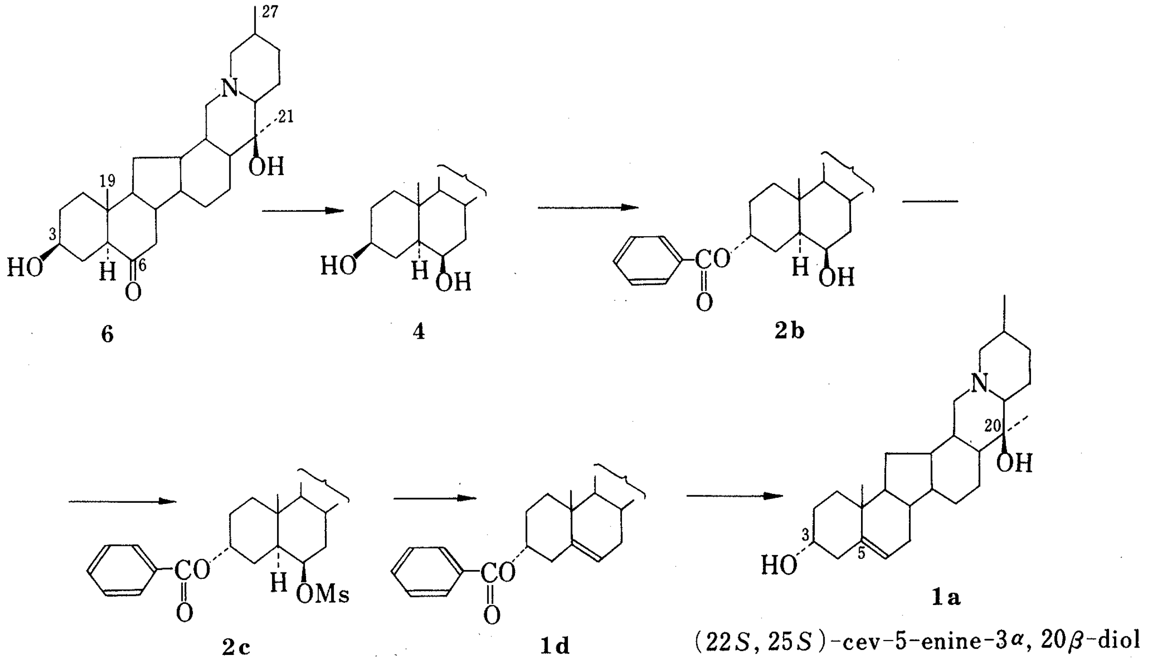

Chart 1

On the basis of fact that **1a** was isolated only from the aerial part, in addition to **2a** and **3**, it seems reasonable to suggest that **1a** and 5α-cevanine alkaloids having a 3α-hydroxyl group, such as **2a** and **3**, are synthesized through quite a similar biogenetic pathway at the aerial part of this plant.

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Received July 21, 1980

[Chem. Pharm. Bull.
28(12)3713—3715(1980)]

Revised Structures of Chebulinic Acid and Chebulagic Acid

The structures of chebulinic acid and chebulagic acid, which were previously formulated as dicarboxylic acids, Ib and IIb, have been revised to monocarboxylactones, Ic and IIc, respectively, on the basis of spectral and chemical evidences.

Keywords——myrobalans; *Terminalia chebula*; Combretaceae; chebulinic acid; chebulagic acid; revised structure; ^{13}C NMR; deuterium-induced differential isotope shift (DIS)

Chebulinic acid (I) and chebulagic acid (II) are the main tannins of myrobalans [fruit of *Terminalia chebula* (Combretaceae)]. Their structures were firstly formulated as Ia and

IIa,[1] and then revised to dicarboxylic acids, Ib and IIb.[2] The structure of terchebin which is another tannin constituent of myrobalans has been recently revised.[3]

We have now reinvestigated the structures of I and II. ^{13}C Nuclear magnetic resonance (^{13}C NMR) spectrum of I exhibited five signals at 141.39—140.05 ppm, four of which were assigned to those of C-4‴ in the three galloyl groups, and C-5′ (C), based on the data of the related compounds.[4,5] An additional signal in this region might be regarded as that of C-6′ or C-4′ which was shifted upfield from the expected region around 147 ppm. Upon the

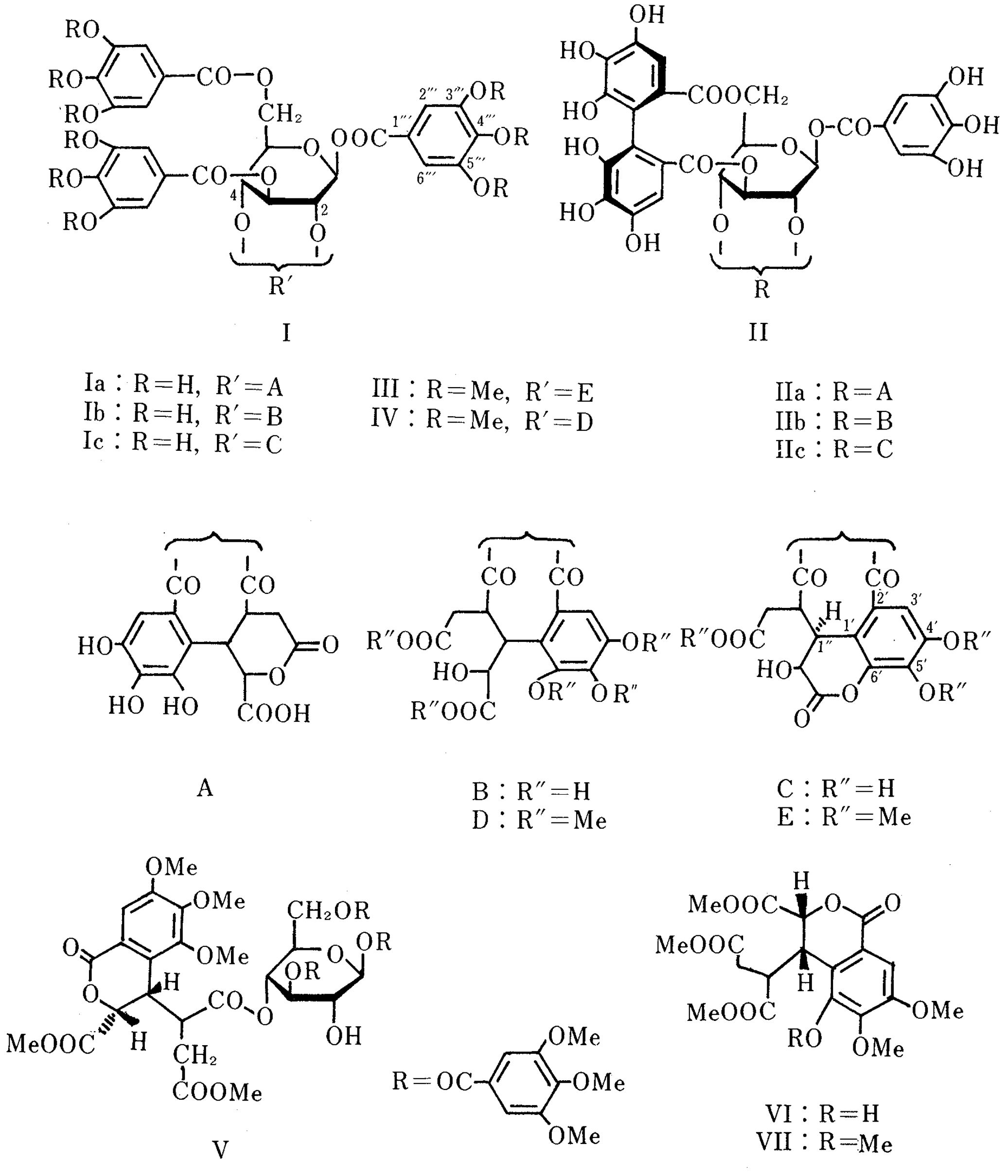

Chart 1

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1) O.T. Schmidt, *Fortschr. Chem. Org. Naturstoffe*, **13**, 70 (1956).
2) *a*) E. Haslam and M. Uddin, *J. Chem. Soc.* (*C*), **1967**, 2381; *b*) J.C. Jochims, G. Taigel, and O.T. Schmidt, *Ann.*, **717**, 169 (1968).
3) T. Okuda, T. Hatano, H. Nitta, and R. Fujii, *Tetrahedron Lett.*, **21**, 2561 (1980).
4) T. Okuda, T. Yoshida, and T. Hatano, *Tetrahedron Lett.*, **21**, 2561 (1980).
5) T. Yoshida and T. Okuda, *Heterocycles*, **14**, 1743 (1980).

deuterium-induced differential isotope shift (DIS) measurement,[4–7] the signal at 141.39 ppm was shown as a single peak, while all of the other phenolic carbon signals around 140 and 147 ppm showed definite DIS (0.13—0.23 ppm). This result which is analogous to that observed upon the DIS measurement of geraniin,[4] suggests that the oxygen at C-6′ is not in a free hydroxyl group. The DIS spectrum also showed the dual peak (DIS, 0.23 ppm) for only one carboxyl carbon at 174.98 ppm to indicate formation of a lactone ring between C-6′ and a carboxyl group. Although the ^{1}H NMR spectrum of I in DMSO-d_6 was reported to show a carboxyl peak of two protons,[2] we have observed a carboxyl peak of one proton rather than two. In addition, presence of a lactone in I was supported by ^{13}C NMR in the presence of Et_3N (2.5 mol eq), as only one carboxyl signal at 174.98 ppm showed significant downfield shift by 3.7 ppm upon the formation of the carboxylate salt. The infrared (IR) spectrum of I shows a distinct shoulder at 1775 cm^{-1} in addition to a broad band at 1700—1730 cm^{-1}. This shoulder peak is now attributable to dihydrocoumarin ring which was once mentioned by Haslam without determining a structure consistent with this observation.[2a] These findings exclude structures Ia and Ib for chebulinic acid, and are compatible with the alternative monocarboxylactone structure Ic.

The methylation of I with CH_2N_2 was reported to give tetradecamethyl derivative which supports structure Ib of chebulinic acid.[2a] This reaction has now been re-examined as follows. The methylation of I for 3 hr gave dodecamethyl chebulinic acid (III), accompanied by tetradecamethyl chebulinic acid (IV). These products were transformed into tetradecamethyl neochebulinic acid (V)[1] upon prolonged methylation (*ca.* 10 hr). In the IR spectra of these methylated derivatives, only III showed the distinct shoulder at 1780 cm^{-1} to indicate that only III is the normal methylated derivative of chebulinic acid. The structural assignments of III—V were supported by their methanolysis, upon which pentamethyl chebulic acid (VI) was obtained from III, and hexamethyl chebulic acid (VII)[8] from both of IV and V.

Chebulagic acid (II) showed the DIS spectrum which is similar to that of I. Based on this result and the distinct shoulder at 1775 cm^{-1} in the IR spectrum, structure IIb for chebulagic acid also has been revised to IIc.

The absolute configuration at C-1″ is tentatively assigned as shown in Ic and IIc, by biogenetic considerations of their coexistences with terchebin[3] in the same plant. The atropisomerism at the hexahydroxydiphenoyl (HHDP) group in II is *R*, as hydrolysis of II gives corilagin,[9] in which the atropisomerism at the HHDP group was recently established to be *R*.[4]

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Received September 8, 1980

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6) Taken in acetone-d_6–H_2O (D_2O) (7 : 3) with dual tube consisting of 8 mm OD and 5 mm OD tubes.
7) P.E. Pfeffer, K.M. Valentine, and F.W. Parrish, *J. Amer. Chem. Soc.*, **101**, 1265 (1979).
8) O.T. Schmidt and W. Mayer, *Ann.*, **571**, 1 (1951).
9) O.T. Schmidt and D.M. Schmidt, *Ann.*, **578**, 25 (1952).