von IV′ um 0.6 ppm zu höherem Feld verschoben. Damit wird dem zweiten Glykoside die Struktur (II) eines Pterosin C-3-β-L-Arabinopyranosids zugeordnet.

Aus CD-Daten ergibt sich, dass es sich bei I und II um Gemische von 2,3-*trans* (2*S*, 3*S*)- und 2,3-*cis* (2*S*, 3*R*)[5]-Isomeren handelt.

Von den drei Glykosiden aus *P. oshimensis* HIERON. Pterosin Q-3-β-L-Arabinopyranosid, Pterosin Q-3-β-D-Glukopyranosid und Pterosin C-3-β-L-Arabinopyranosid, war das erstere ein Hauptglykosid und die letzteren zwei wurden in nur geringer Menge erhalten.

Das Pterosin Q-3-β-L-Arabinopyranosid konnten wir auch aus *Histiopteris incisa* (THUNB.) J. SMITH isolieren.

Der Eigenname Pterosid Q[2] für Pterosin Q-3-β-D-Glukopyranosid ist aus der Literatur zu streichen.

Danksagung Wir danken Herrn M. Satake, National Institute of Hygienic Sciences für die Hilfe bei der Suche und Sammlung des Pflanzenmaterials.

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[5] S. Natori und Mitarbb. (*Chem. Pharm. Bull.* (Tokyo), **22**, 2762 (1974)) haben dem 2,3-*cis*-Pterosin C die (2*R*,3*S*)-Konfiguration zugeordnet.

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Isolation and Characterization of 10,11-Dihydroatlantone and Related Compounds from *Ginkgo biloba* L.

E- and Z-forms of 10,11-dihydroatlantone and its 6-oxo-compound were newly isolated in optically inactive form from heart wood of *Ginkgo biloba* L. These structures were confirmed by synthesis stating from limonene.

In continuing investigation of the neutral portion of an extract from heart-wood of *Ginkgo biloba* L.,[1] we report here isolation and characterization of dihydroatlantone and related sesquiterpenes.

By way of column and preparative thin-layer chromatographies using silica gel and silica gel impinged with silver nitrate, four oily compounds, A, B, C, and D were isolated from much faster running eluate than bilobanone (I)[1] which was the main constituent of the essential oil obtained from this heart-wood. Both A and B were optically inactive and the same molecular weight, $M^+=220$ corresponding to $C_{15}H_{24}O$ and showed *m/e* 57 (base peak, $C_4H_9^+$) in their mass spectra and a carbonyl band at 1670 cm^{-1} in their infrared (IR) spectra. The nuclear

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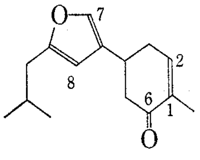
[1] H. Irie, H. Kimura, N. Otani, K. Ueda, and S. Uyeo, *Chem. Commun*, 1968, 678; H. Kimura, H. Irie, K. Ueda, and S. Uyeo, *Yakugaku Zasshi*, **88**, 562 (1968).

magnetic resonance (NMR) spectra of these two compounds exhibited the following signals: A; δ ($CDCl_3$) 0.91 (6H, d., $J=6.5$ Hz), 1.64 (3H, broad s.), 1.78 (3H, d., $J=1.5$ Hz), 3.70 (1H, m.), 5.34 (1H, m.), and 5.91 (1H, q., $J=1.0$ Hz), B; 0.91 (6H, d., $J=6.5$ Hz), 1.64 (3H, broad s.), 2.09 (3H, d., $J=1.5$ Hz), 5.35 (1H, m.), and 5.96 (1H, q. $J=1.0$ Hz). Furthermore, A and B were interconvertible, because each of pure A and B gave a mixture of A and B on standing several days at room temperature (gas chromatographic examination).

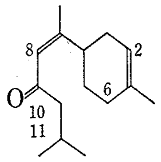
Considering the spectroscopic evidence and the structure of bilobanone, A and B were proposed as Z- and E-forms of 10,11-dihydroatlantone (II) and (III), respectively. The low field shift of one (δ 2.09) of the olefinic methyl of B corresponding to an olefinic methyl (δ 1.78) of A was explained by the anisotropic effect of the carbonyl group. Confirmation of this proposal was provided by synthesis of E-form of 10,11-dihydroatlantone (III). Thus, treatment of limonene (IV) with butyllithium by Crawford method[2] followed by isovaleraldehyde gave the alcohol (V), Jones' oxidation of which yielded the ketone (VI).[3] Isomerization of an exomethylene double bond of (VI) with alumina in ether furnished E-form of 10,11-dihydroatlantone (III) which was identical with B in our hands spectroscopically and chromatographically (thin–layer and gas chromatographies) and also gave a mixture of A and B on standing. Therefore, A was firmly proposed as Z-form (II) of 10,11-dihydroatlantone. This is the first isolation of E- and Z-forms of dihydroatlantone from natural source.

C and D were also interconvertible and showed virtually identical mass spectra. Since the NMR and IR spectra of the former were superimposable upon those of E-atlantone kindly supplied by Dr. Crawford, D should be Z-atlantone.

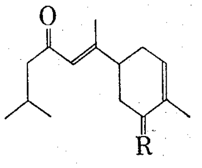
From much slower running eluate than bilobanone, β-eudesmol, γ-eudesmol, elemol and a new substance E (optically inactive) were obtained. Charactrization of all the known compounds was provided by direct comparison of their NMR and IR spectra with those of authentic spectra. The new substance E showed a band at 1660 cm^{-1} in its IR spectrum and the signals at δ ($CDCl_3$) 0.92 (6H, d, $J=6.5$ Hz), 1.79 (3H, d., $J=2.8$ Hz), 2.16 (3H, d., $J=2.0$ Hz), 6.08 (1H, m.), and 6.75 (1H, m.) in its NMR spectrum, and M^+ 234 and m/e 57 (base peak) in its mass spectrum, indicating the presence of the conjugated ketone, isobutyl side chain and two olefinic bonds. The signal of an olefinic proton at δ 6.08 was quite similar to that of C_8–H of III in the respects of the chemical shift and the shape. The other olefinic proton signal at δ 6.75 was closely related with that of C_2–H of bilobanone (I). Based on the above similarity, the structure of E was culminated in E-form of 10,11-dihydro-6-oxo-atlantone (VII) which was a new bisabolene type sesquiterpene. Synthesis of (VII) was completed by oxidation of III with chromium trioxide–pyridine complex in methylenchloride,[4] confirming the structure.



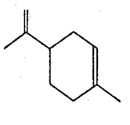
I



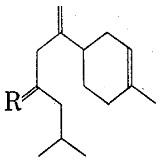
II



III : R=H_2
VII : R=O



IV



V : R=OH, H
VI : R=O

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[2] R.J. Crawford, W.F. Erman, and C.D. Broaddus, *J. Am. Chem. Soc.*, **94**, 4298 (1972).

[3] All the compounds cited in this report were satisfactorily purified under gas chromatographic examination and showed adequate mass spectra.

[4] W.G. Dauben, M. Lorber, and D.S. Fullerton, *J. Org. Chem.*, **34**, 3587 (1969).

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Cannabichromevarin and Cannabigerovarin, Two New Propyl Homologues of Cannabichromene and Cannabigerol[1]

Two new neutral cannabinoids, cannabichromevarin and cannabigerovarin, were isolated from the "Meao variant," Thailand Cannabis and their structures were determined to be the homologues of cannabichromene and cannabigerol which have a propyl side-chain, respectively, on the basis of spectral and chemical evidences.

In recent years much research has been directed towards the isolation and identification of propyl homologues of cannabinoids from local *Cannabis*,[2–5] such as cannabidivarin (CBDV),[2] tetrahydrocannabivarin (THCV)[3] and cannabivarin (CBV).[4]

We now wish to describe the isolation and the structure elucidation of two new neutral cannabinoids, the homologues of cannabichromene (CBC) and cannabigerol (CBG) which have a propyl side-chain from the "Meao variant," Thailand *Cannabis*.

After the benzene percolate of the leaves harvested in the vegetative phase was decarboxylated by heating at 160° for 20 min, the neutral cannabinoids fraction was repeatedly column-chromatographed over silica gel with solvent benzene or benzene–hexane–diethyl amine (20:10:1) to give four propyl homologues besides the usual neutral cannabinoids. Two propyl homologues were identified with CBDV[2] and THCV.[3] The third new cannabinoid (I) gave a brownish red color with diazotized benzidine and the physical constants were as follows; I, $C_{19}H_{26}O_2$ (Calcd.: 286.193, Found: 286.191), colorless oil, $[\alpha]_D^{19}$ +58° (c=4.28, $CHCl_3$), UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (ε): 281 (7577), 289 (7192, shoulder), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3320 (OH), 1623, 1576 (C=C), 1430, 1090, 1040, NMR (in $CDCl_3$) δ: 0.92 (3H, triplet, ω-CH_3), 1.26 (3H, singlet, C_{10}–CH_3), 1.58, 1.67 (3H×2, each singlet, $C_{8,9}$–CH_3), 2.45 (2H, triplet, α-CH_2), 5.10 (1H, triplet, C_6–H), 5.45 (1H, doublet, J=10 Hz, C_2–H), 6.12, 6.26 (1H×2, each singlet, $C_{3',5'}$–H), 6.62 (1H, doublet, J=10 Hz, C_1–H), Mass Spectrum *m/e*: (M^+) 286 (7.2%), 271 (3.8%), 204 (15.8%), 203 (100%), 187 (3.3%), 174 (12.8%).

The nuclear magnetic resonance (NMR) is similar to CBC[6,7] except for the methylene region and the mass spectrum (MS) has a characteristic fragmentation pattern of CBC,[7] with the differenciation that all masses are 28 unit (C_2H_4) smaller. All of the properties of I

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[1] This forms part IX of "Cannabis." Part VIII: Y. Shoyama, M. Yagi, T. Yamauchi, and I. Nishioka, *Phytochemistry*, in press.
[2] L. Vollner, D. Bieniek, and F. Korte, *Tetrahedron Letters*, **1969**, 145.
[3] E.W. Gill, *J. Chem. Soc.*, **1971**, 579.
[4] F.W.H. Mercus, *Nature*, **232**, 579 (1971).
[5] P.S. Fetterman and C.E. Turner, *J. Pharm. Sci.*, **61**, 1476 (1972).
[6] Y. Gaoni and R. Mechoulam, *Chem. Commun.*, **1966**, 20.
[7] U. Claussen, F.V. Spulak, and F. Korte, *Tetrahedron*, **22**, 1477 (1966).