and recently, Kametani, *et al.*[3] and Battersby, *et al.*[4] also reported the synthesis of the spiro-dienone system under the same conditions following that of Hey, *et al.* However, there has been no report that the deamination of 8-aminoisoquinoline gives the spiro-dienone system, proaporphine.

Further investigation on the deamination of 8-aminoisoquinolines is in progress in this laboratory.

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Tokyo College of Pharmacy,
Kashiwagi, Shinjuku-ku, Tokyo

SABURO ISHIWATA
KEIICHI ITAKURA

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3) T. Kametani, K. Fukumoto, and T. Sugahara, *Tetrahedron Letters*, **52**, 5459 (1968).
4) A.R. Battersby, A.K. Bhatnagar, P. Hackett, C.W. Thornber, and J. Stauton, *Chem. Commun.*, **1968**, 1214.

[Chem. Pharm. Bull. 17(6)1299—1301(1969)]

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Structures of New Flavonoids, Sophoradin and Sophoranone, from *Sophora subprostrata*

During the course of our studies on the constituents of the root of *Sophora subprostrata* CHUN et T. CHEN (Chinese Drug: Shan-Dou-Gen (山豆根)), two new flavonoids, sophoradin (I) and sophoranone (VIII), (both named by us), have been isolated from the ether-soluble fraction of the methanol extract.

In this communication, we wish to report the structures of these flavonoids.

Sophoradin (I) was obtained as yellow needles; mp 161°; $C_{30}H_{36}O_4$; $FeCl_3$ (+); UV λ_{max}^{EtOH} mμ (log ε): 380 (4.60), $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ (log ε): 480 (4.70); IR (KBr) cm^{-1}: 3400, 3200 (OH), 1635 (conjugated CO), 1610 (aromatic C=C), 1380 ($-CH_3$).

The UV spectrum suggested the presence of chalcone nucleus in I,[1a] which was also supported by the formation of a dihydrochalcone derivative (II) (octahydrosophoradin), mp 102°, $C_{30}H_{44}O_4$; UV λ_{max}^{EtOH} mμ (log ε): 288 (4.22); IR (KBr) cm^{-1}: 3500(OH), 1630 (conjugated CO), 1610, 1600 (aromatic C=C), 1385, 1375 ($-CH_3$), by catalytic hydrogenation.

On acetylations, I and II gave each of the triacetates, III[2]; $FeCl_3$ (—); NMR[3]: 7.70 (6H, s., –OAc×2), 7.75 (3H, s., –OAc), and IV[2]; $FeCl_3$ (—); NMR: 7.72 (9H, s., –OAc×3).

The NMR spectrum of I shows the presence of three γ,γ-dimethylallyl groups: 8.20 (18H, s., $-C{=}C\langle^{CH_3}_{CH_3}\times 6$), 4.70 (3H, br. t., J=6 cps, $-CH_2-\underline{C}H{=}C\langle\times 3$), 6.65 (6H, br. d., J=6 cps, $Ar-\underline{C}H_2-CH{=}C\langle\times 3$). Furthermore, these signals in I disappeared in II, while a sharp doublet

1) *a*) L. Jurd, "The Chemistry of Flavonoid Compounds," T.A. Geissman, ed., Pergamon Press, London, 1962, pp. 141—147; *b*) W.A. Whalley, *ibid.*, pp. 441—467.
2) The product was failed to be crystallized, but its purity was certified by thin-layer chromatography.
3) All NMR spectra were taken at 60 Mcps in $CDCl_3$ with TMS as an internal standard. Chemical shifts were given in τ values. Abbreviations: s.; singlet, d.; doublet, t.; triplet, m.; multiplet, br.; broad.

at 9.05 (18H, J=6 cps, $-CH\langle^{CH_3}_{CH_3}\times 6$), a broad multiplet at 8.6 (6H, $-C\underline{H}_2-C\underline{H}\langle\times 3$) and a broad triplet at 7.5 (6H, J=7.5 cps, $Ar-CH_2-C\underline{H}_2-\times 3$) appeared in II.

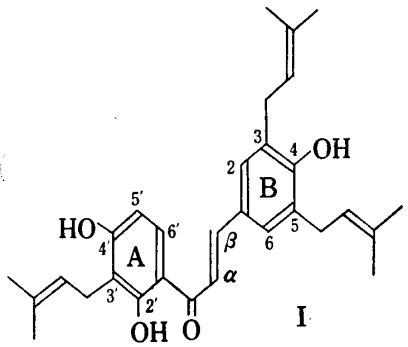
These facts indicate that I must be a trihydroxy-triisopentenyl chalcone.

Cleavage of I with 50% KOH gave a acetophenone derivative which would be derived from A-ring, and having the physical properties in full accord with V: mp 160° (lit.[4] mp 155—156°); $C_{13}H_{16}O_3$; IR (KBr) cm^{-1}: 3120 (OH), 1630 (conjugated CO), 1595 (aromatic C=C), 1380 ($-CH_3$); UV λ_{max}^{EtOH} mμ: 287; NMR: 8.26 (3H, s., $C=C\langle^{CH_3}_{C}$), 8.20 (3H, s., $C=C\langle^{C}_{CH_3}$), 7.46 (3H, s., $Ar-COC\underline{H}_3$), 6.6 (2H, d., J=7 cps, $Ar-C\underline{H}_2-CH=C\langle$), 4.75 (1H, t., J=7 cps, $-CH_2-C\underline{H}=C\langle$), 3.84 (1H, s., C-4-O$\underline{H}$), 3.66 (1H, d., J=9 cps, C-5-H), 2.51 (1H, d., J=9 cps, C-6-H), —3.1 (1H, s., C-2-O$\underline{H}$).

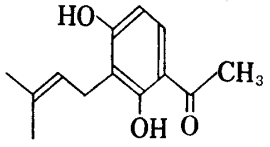
In the UV spectrum of I, a bathochromic shift of 100 mμ and an increase in intensity were observed on the addition of sodium ethoxide, indicating that the remaining a hydroxyl group must be placed at position 4.[1a)]

In the NMR spectrum of I, two pair of AB type quartets centred at 2.30, 3.62 (J=8 cps) and 2.20, 2.65 (J=15 cps) were assigned to C-6′,5′-H and olefinic protons of chalcone nucleus (C-β,α-H), respectively, showing that the remaining two isopentenyl groups in I must be on the B-ring. And the two aromatic protons of B-ring of I and its derivatives appeared as equivalent singlets in each cases: I, 2.75; II, 3.32; III, 2.85; and IV, 3.03.

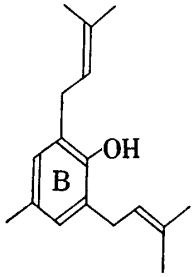
These facts led to the two possible partial formulae, Ia and Ib, for the B-ring.



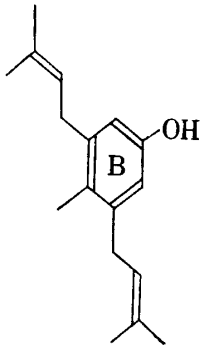
I



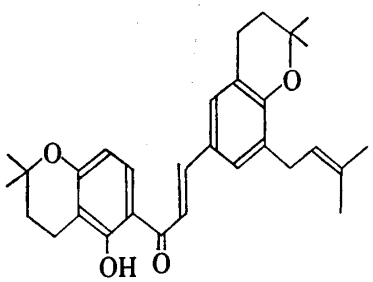
V



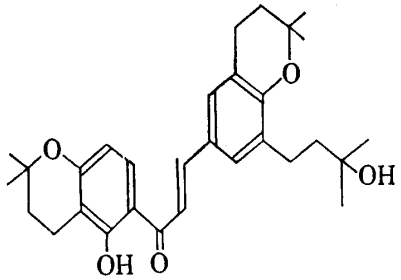
Ia



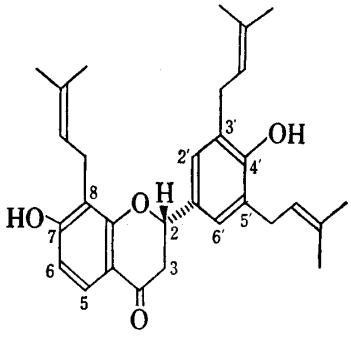
Ib



VI



VII



VIII

On refluxing a solution of I in methanolic hydrochloric acid, the isopentenyl side chains were cyclized to form some kinds of dichromans, out of which two compounds were isolated and formulated as VI and VII from their spectral characteristics: VI[2)]—UV λ_{max}^{EtOH} mμ: 382;

4) V.K. Bhalla, U. Ramdas Nayak, and Sukh Dev, *Tetrahedron Letters*, **1968**, 2401.

$\lambda_{max}^{EtOH-AlCl_3}$ mμ: 440; NMR: 8.65 (12H, s., $-\underset{-O}{\overset{-C}{>}}C<\underset{CH_3}{\overset{CH_3}{}}\times 4$), 8.30 (6H, d., J=1 cps, $-C{=}C<\underset{CH_3}{\overset{CH_3}{}}\times 2$), 8.1—8.4 (4H, m., $-C\underline{H}_2-\times 2$), 7.3 (4H, m., $Ar-C\underline{H}_2-CH_2\times 2$), 6.8 (2H, d., J=6 cps, $Ar-C\underline{H}_2-CH{=}C<$), 4.8 (1H, t., J=6 cps, $-CH_2-C\underline{H}{=}C<$), 3.7 (1H, d., J=9 cps, C-5′-H), 2.8 (2H, s., C-2, 6-H), 2.63 (1H, d., J=15 cps, C-α-H), 2.35 (1H, d., J=9 cps, C-6′-H), 2.22 (1H, d., J=15 cps, C-β-H), —4.2 (C-2′-OH). VII—yellow needles; mp 145°; $C_{30}H_{38}O_5$; UV λ_{max}^{EtOH} mμ: 382; $\lambda_{max}^{EtOH-AlCl_3}$ mμ: 440; NMR: 8.71 (6H, s., $HO\overset{C}{>}C<\underset{CH_3}{\overset{CH_3}{}}\times 2$), 8.65 (12H, s., $-\underset{-O}{\overset{C}{>}}C<\underset{CH_3}{\overset{CH_3}{}}\times 4$), 8.3 (6H, m., $-CH_2-\times 3$), 7.3 (6H, m., $Ar-C\underline{H}_2<\times 3$), 3.6 (1H, d., J=9 cps, C-5′-H), 2.69 and 2.71 (2H, d., J=2 cps, C-2,6-H), 2.55 (1H, d., J=15 cps, C-α-H), 2.25 (1H, d., J=9 cps, C-6′-H), 2.15 (1H, d., J=15 cps, C-β-H), —4.21 (1H, s., C-2′-O$\underline{H}$).

This result could rule out the possibility of partial formula (Ib) which must give only monochroman system.

From these findings, the structure of sophoradin could be assigned as I.

Sophoranone (VIII) was obtained as colorless needles, mp 108°, $C_{30}H_{36}O_4$. Physical properties: $[\alpha]_D^{25}$ —13.0 (*c*, 0.5 in EtOH); UV λ_{max}^{EtOH} mμ (log ε): 286 (4.14); IR (KBr) cm^{-1}: 3300 (OH), 1660 (conjugated CO), 1600 (aromatic C=C); NMR: 8.37 (6H, s., $C{=}C<\underset{CH_3}{\overset{CH_3}{}}\times 2$), 8.24 (12H, s., $C{=}C<\underset{CH_3}{\overset{CH_3}{}}\times 4$), 7.2 (2H, m., C-3-$\underline{H}_2$), 6.7 (6H, d., J=7 cps, $Ar-C\underline{H}_2-CH{=}C<\times 3$), 4.8 (4H, m., C-2-H and $-CH_2-C\underline{H}{=}C<\times 3$), 4.48 (1H, s., -O$\underline{H}$), 3.45 (1H, d., J=8 cps, C-6-H), 3.04 (2H, s., C-2′,6′-H), 2.40 (1H, d., J=8 cps, C-5-H), 1.4 (1H, s., -O$\underline{H}$).

VIII was considered to be the flavanone corresponding to I from its spectral characteristics. VIII was readily cleaved with 10% NaOH to give I. Furthermore, refluxing I in anhydrous pyridine containing some piperidine regenerated (±)-sophoranone (VIII′), mp 108°, which exhibited no optical rotation and did not depress the melting point on admixture with natural sophoranone (VIII). Moreover, VIII′ shows the spectra (IR, UV and NMR) which are hardly distinguishable from those of natural sophoranone.

Since the reasonable suggestion has been made that probably all (—)-flavanone have S-chirality at C-2,[1b] sophoranone could be formulated as VIII.

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Research Laboratory,
Taisho Pharmaceutical Co., Ltd.,
Takata 3-chome, Toshima-ku, Tokyo

MANKI KOMATSU
TSUYOSHI TOMIMORI
KATSUO HATAYAMA
YUKIKO MAKIGUCHI
NAOKO MIKURIYA

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