Communications to the Editor

[Chem. Pharm. Bull. 33(8)3545—3547(1985)]

TWO NOVEL AROMATIC COMPOUNDS FROM CAESALPINIA SAPPAN

Takashi Shimokawa,[a] Jun-ei Kinjo,[a] Johji Yamahara,[b] Masaki Yamasaki,[c] and Toshihiro Nohara*,[a]

Faculty of Pharmaceutical Sciences, Kumamoto University,[a] Oe-honmachi 5-1, Kumamoto 862, Japan, Kyoto College of Pharmacy,[b] Nakauchi-cho 5, Misasagi, Yamashina-ku, Kyoto 607, Japan, and Department of Biochemistry, Medical School, Kumamoto University,[c] Honjo, Kumamoto 860, Japan

Two novel aromatic compounds named caesalpins J and P were isolated from Sappan Lignum, the dried heartwood of Caesalpinia sappan L. (Leguminosae), and their structures were deduced by spectroscopy. Their chemical structures are related to 3-benzyl-chroman compounds and brazilin.

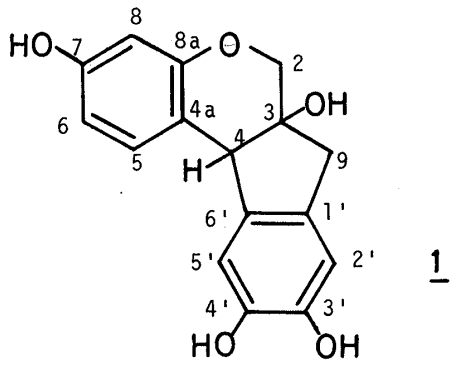
KEYWORDS —— Caesalpinia sappan; Sappan Lignum; Leguminosae; caesalpin J; caesalpin P; brazilin; 3-benzyl-chroman derivative; antihypercholesteremic activity

Sappan Lignum, the dried heartwood of Caesalpinia sappan L. (Leguminosae) is known as an oriental crude drug used, for example, as an anti-inflammatory agent.[1] In the course of a systematic screening for antihypercholesteremic activity, the methanolic extractive of this plant was shown to have a significant effect. From this extractive, we obtained seventeen aromatic compounds together with brazilin (1)[2] and sappanchalcone,[3] and reported the chemical characterization of eight of them.[4] The present paper deals with the essential data leading to the assignment of the structures 2 and 3, designated as caesalpins J and P (Yields: 0.28, 0.01%, respectively), to two novel compounds, which offer new framework-models for the naturally occurring compounds.

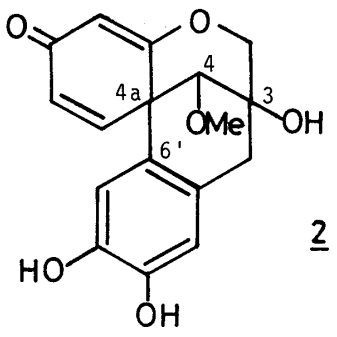
Caesalpin J (2), colorless needles, mp 242-243°C (dec.), $[\alpha]_D$ +445.0° (MeOH), showed a peak at m/z 316 originating from the molecular ion $C_{17}H_{16}O_6^+$ in the MS. The IR spectrum exhibited absorptions due to the α,β-unsaturated ketone at 1660 cm^{-1} and an aromatic ring at 1590 cm^{-1}, along with a strong hydroxyl group at 3400 cm^{-1}. The ^{13}C-NMR spectrum (Table I) showed signals due to a tatal of seventeen carbons composed of the following functional groups: a methoxyl group, an α,α',β,β'-unsaturated ketone system, a methylene bearing the oxygen atom, two quaternary carbons, one benzyl carbon, a methylene adjacent to the oxygen function, and six aromatic carbons. In a comparative study of the ^1H-NMR spectra (in DMSO-d_6) of 2 and 1, a signal in 2 at δ 5.42 assignable to 8-H on the aromatic ABX system (1H, d, J=10 Hz, δ 6.98; 1H, dd, J=2,10 Hz, δ 6.36; 1H, d, J=2 Hz, δ 5.42) shifted toward the high field by 0.78 ppm, indicating that the carbonyl group is located at C-7, which is conjugated to two double bonds (C_5=C_6 and C_8=C_{8a}). Moreover, two broad singlet signals (each 2H) at δ 3.10 and 4.03 were assigned to 9-H_2 and 2-H_2, and two aromatic

protons at δ 6.30 and 6.53 (each1H, s) were due to 2'-H and 5'-H. Since one (δ 68.0) of two quaternary carbon signals in the ^{13}C-NMR spectrum of 2 was most likely attributable to C-3 in relation to the structure of 1, the other (δ 52.0) should be assigned to C-4a. The remaining methine carbon [carbon, δ 83.6 (d) and methine proton, δ 3.80 (s)] was thus assignable to C-4. The ^{1}H-NMR spectrum of the diacetate of 2 derived by the usual acetylation showed two phenolic acetoxyl groups at δ 2.27, suggesting that the methoxyl group is linked to C-4. From the above evidence, the structure of 2 was constructed as shown in the formula, in which C-4a centre took a spiroform having a new C-C linkage between C-4a and C-6'. However, the stereochemistry at C-3, 4 and 4a remains unsolved. It was supposed that 2 was formed from compound 4,[4a] obtained earlier as a key-intermediate in the biogenesis of 1, by oxidative coupling between C-4a and C-6'.

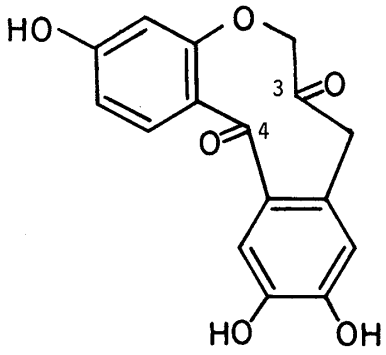
Caesalpin P (3), colorless plates, mp 216-218°C, $[\alpha]_D$ ±0° (MeOH), exhibited a molecular ion at m/z 300 in the MS to give a molecular formula $C_{16}H_{12}O_6$, suggesting 3 to be a compound related to 1. The IR spectrum showed another ketone group (1710 cm^{-1}) along with the enone group (1625 cm^{-1}, sh.). Two singlet signals at δ 4.72 (2H, s), and 3.53 (2H, s) in the ^{1}H-NMR spectrum (in DMSO-d_6) was assigned to 2-H and 9-H, respectively, by referring to those signals in 1. Five aromatic protons resonated at δ 7.72 (1H, d, J=9 Hz), 6.69 (1H, dd, J=2,9 Hz), 6.68 (1H, d, J=2 Hz), 6.48 (1H, s) and 7.15 (1H, s). The first three of these (aromatic ABX type system) were ascribed to 5-H, 6-H and 8-H, and the last two to 2'-H and 5'-H. The ^{13}C-NMR spectrum of 3 showed two ketone groups at δ 190.2 and 206.7. In connection with the evidence of the ^{1}H-NMR data, these two ketone groups were located at C-3 and C-4. Owing to orientation of the ketone group at the para-location, the signals at C-7 and C-3' shifted downfield by 9.6 and 4.0 ppm compared with those of the ^{13}C-NMR spectrum of 1. This evidence also indicates the presence of a carbonyl group at C-4. Robinson et al. had obtained synthetically from 1 a compound



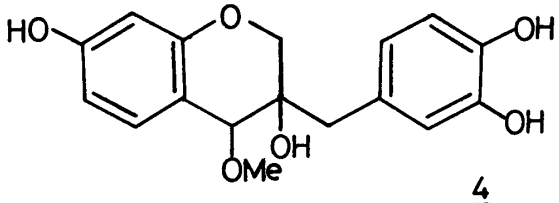
1



2



3



4

Table I. ^{13}C-NMR Data for Compounds 1-4 (in DMSO-d_6)

Carbon	1	2	3	4
2	69.5 t	74.8 t	76.5 t	66.7 t
3	76.3 s	68.0 s	206.7 s	78.3 s
4	49.4 d	83.6 d	190.2 s	69.5 d
4a	114.2 s	52.0 s	123.0 s[a)]	112.1 s
5	130.8 d	148.0 d	132.0 d	132.2 d
6	108.7 d	129.7 d	112.0 d	107.9 d
7	153.9 s	187.8 s	163.5 s	158.9 s
8	102.7 d	108.6 d	105.5 d	102.5 d
8a	156.4 s	174.9 s	159.7 s	154.1 s
9	41.8 t	42.4 t	46.5 t	--
1'	129.7 s	123.7 s	132.4 s	127.2 s
2'	112.0 d	115.2 d	116.2 d	114.9 d
3'	144.1 s	145.5 s	148.1 s	144.7 s
4'	143.8 s	143.7 s	144.0 s	143.7 s
5'	111.6 d	112.7 d	117.7 d	118.2 d
6'	135.5 s	125.6 s	123.1 s[a)]	121.4 d
OMe		61.1 q		56.6 q

a) This assignment may be interchanged.
-- hidden by solvent.

designated as brazilone triacetate[5)] corresponding to the triacetyl derivative of 3. The triacetate of 3 was identified as the brazilone triacetate derived from 1 by the above method.[5)] Therefore, the structure of 3 is represented as shown in the formula. Since the two substances obtained here were contained in the original extractive as indicated by TLC, it appears that they were not artifacts produced by the separation procedure. They present new examples of a novel skeleton among the naturally occurring compounds. A total survey of the constituents and their chemical correlation in Caesalpinia sappan is now in progress.

ACKNOWLEDGEMENT The authors are grateful to Prof. T.Tomimatsu, Faculty of Pharmaceutical Sciences, Tokushima University, for measurements of the MS, ^{1}H- and ^{13}C-NMR spectra.

REFERENCES

1) Chiang Su New Medical College ed., "Dictionary of Chinese Crude Drugs," Shanghai Scientific Technologic Publisher, Shanghai, 1977, p.1083.
2) J.C.Craig, A.R.Naik, R.Pratt, E.Johnson and N.S.Bhacca, J. Org. Chem., 30, 1573 (1965).
3) M.Nagai, S.Nagumo, I.Eguchi, S.Lee and T.Suzuki, Yakugaku Zasshi, 104, 935 (1984).
4) a) C.Fuke, J.Yamahara, T.Shimokawa, J.Kinjo, T.Tomimatsu and T.Nohara, Phytochemistry, in press; b) The 105 th Annual Meeting of Pharmaceutical Society of Japan, Kanazawa, Apr., 1985, p.466.
5) F.Morsingh and R.Robinson, Tetrahedron, 26, 281 (1970).

(Received May 18, 1985)