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THE STRUCTURES OF AH₁₅ AND AH₁₈, NEW BI- AND TRI-PHENYLETHYLCHROMONES
FROM AGALWOOD

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New bi- and tri-2-(2-phenylethyl)chromones, tentatively named AH₁₅
and AH₁₈ were isolated from Agalwood "Jinkō" and their structures were
determined.

KEYWORDS— bi-2-(2-phenylethyl)chromone; tri-2-(2-phenylethyl)-
chromone; agalwood; Aquilariaceae; ¹H-NMR; ¹³C-NMR

New bi- and tri-2-(2-phenylethyl)chromones, AH₁₅ and AH₁₈ were isolated from
the acetone extracts of agalwood "Jinkō" from Kalimantan, along with other related
compounds.¹⁾

This paper describes the characterization of these structures.

AH₁₅, C₃₄H₃₀O₉, colorless needles, mp 244-245°C, [α]_D +5.8° (MeOH) appeared to
be a bi-2-(2-phenylethyl)chromone derivative according to their IR (KBr), UV (MeOH)
and ¹H-NMR spectra : 1668, 1625, 1590 cm⁻¹ and 244 nm, ε = 36321 (γ-pyrone ring); δ
6.11, 6.16 (each s, 3-H). The structure of monomeric one (Unit A) of the dimer
appeared to be agarotetrol on the basis of four methine proton signals at δ 3.89,
4.33, 4.59 and 5.34, and the vicinal coupling systems of 5/6 trans, 6/7 cis, and
7/8 trans (Table I). The doublet signal of the methine proton in the downfield po-
sition at δ 5.34 should be assigned to 5-H because of the effect of bonding of the
ether at C₅ to another monomeric unit (Unit B), as in the case of AH₁₀.^{1c)}

The structure and the assignments of protons of Unit B were elucidated by
measuring the nuclear Overhauser effect (NOE) difference and ¹H-¹³C shift-corre-
lated spectra. Irradiation of the 5-H at δ 5.34 gave appreciable NOE increase of
the 5'-H as a well defined doublet signal at δ 7.23 and further irradiation of 5'-
H indicated an NOE increase of 8'-H along with an increase of 5-H. The presence
of the hydroxyl group linked at 7'-position was confirmed by the respective irradi-
ation of phenolic and aquatic protons at δ 9.95 and 3.40 which gave an NOE increase
of 8'-H.

Accordingly, the structure of Unit B was assumed to be a 6,7-disubstituted
one. The above results and the ¹³C-NMR spectrum support the conclusion that AH₁₅
is (5S,6S,7R,8S)-2-(2-phenylethyl)-6,7,8-trihydroxy-5,6,7,8-tetrahydro-5-[2-(2-

phenylethyl)-7-hydroxy-chromonyl-6-oxy]chromone, 1.

AH₁₈ (2), C₅₁H₄₆O₁₄, a white powder (mp 147-148°C), [α]_D -109.1° (MeOH), IR (KBr): 1658, 1600 cm⁻¹, UV (MeOH): 250 nm, ε = 39215 showed peaks at m/z 883 (M⁺H) and 905 (M⁺+Na) in the FD-MS. The ¹H-NMR spectrum of 2 (300 MHz, in DMSO-d₆) showed three proton signals at δ 6.107, 6.136, 6.142 (each s, 3-H) and three sets of phenylethyl groups, indicating the structure of a tri-2-(2-phenylethyl)chromone derivative of 2. Two units (Unit C and C') of the trimer appeared to be 5,6,7,8-tetrahydroxy-2-(2-phenylethyl)-5,6,7,8-tetrahydrochromone derivatives, identical with each other because of the presence of the respective pair of the adjacent two proton signals for each proton of the methine and three hydroxyl groups attached to hexenyl ring of the chromone (Table I). The structures of the two units, Unit C and C' were characterized as agarotetrol linked at C₅ by the ether bond to another monomeric unit (Unit D) on the basis of the chemical shifts and coupling systems of the four methine protons similar to those of AH₁₀ and AH₁₅ (Table I).

It appears that the structure of Unit B is 6,7-dialkoxy-2-(2-phenylethyl)chromone, based on the two singlet proton signals (δ 7.85 and 7.73) assumed to be located at the C₅ and C₈ positions of the chromone ring.

The above results were supported by the ¹³C-NMR spectrum, indicating the presence of one pair of signals for each carbon 5-8 position of 5-alkoxy-agarotetrol, and three set signals of C₂, C₄ and C₁'', respectively (Table II).

Accordingly, AH₁₈ was concluded to be bi-(5S,6S,7R,8S)-2-(2-phenylethyl)-6,7,8-trihydroxy-5,6,7,8-tetrahydro-5-[2-(2-phenylethyl)chromonyl-6,7-dioxy]chromone, 2.

AH₁₈ was first isolated from agalwood as the trimer of 2-(2-phenylethyl)chromone. As it relates to the biogenesis of polymerization of 2-(2-phenylethyl)chromones it is noteworthy that these di- and trimers were found to be agarotetrol- and isoagarotetrol-linked at C₅ and C₈ by the ether bond to C₆ and C₇ positions of another monomeric unit, 2-(2-phenylethyl)chromone derivatives, except for the structure of the C-C linkage, AH₁₁.^{1c,d)}

Table I. ^1H -NMR Spectral Data for AH_{15} and AH_{18} (δ in DMSO-d_6)

	AH_{15} (1)		AH_{18} (2)	
	Unit A	Unit B	Unit C and C'	Unit D
5,5'-H	5.34 d $\underline{J}=8.0$	7.23 d $\underline{J}=2.0$	5.41 d $\underline{J}=7.0$ 5.56 d $\underline{J}=7.0$	7.85 s
6-H	4.33 dd $\underline{J}=8.0, 2.0$		4.26 ddd $\underline{J}=7.0, 6.5, 2.0$ 4.35 ddd $\underline{J}=7.0, 6.5, 2.0$	
7-H	3.89 dd $\underline{J}=3.6, 2.1$		3.85 ddd $\underline{J}=4.0, 4.0, 2.0$ 3.89 ddd $\underline{J}=4.0, 4.0, 2.0$	
8,8'-H	4.59 d $\underline{J}=3.7$	6.94 d $\underline{J}=2.0$	4.56 dd $\underline{J}=5.0, 4.0$ 4.59 dd $\underline{J}=5.0, 4.0$	7.73 s
6-OH			5.44 d $\underline{J}=6.5$ 5.48 d $\underline{J}=6.5$	
7-OH		9.95 s	5.31 d $\underline{J}=4.0$ 5.32 d $\underline{J}=4.0$	
8-OH			5.45 d $\underline{J}=5.0$ 5.45 d $\underline{J}=5.0$	
3-H	6.16 s	6.11 s	6.142 s, 6.136 s	6.107 s
CH_2CH_2	2.51 m(4H), 2.94 m(4H)		2.64 m(6H), 2.92 m(6H)	
C_6H_5	6.96 dd $\underline{J}=7.5, 2.0$ 7.17 m(4H), 7.21 m(4H)		6.95 m(3H), 7.12 m(6H), 7.20 m(6H)	

Table II. ^{13}C -NMR Spectral Data for AH_{15} and AH_{18} ^{a)}

	AH ₁₅ (1) (DMSO-d ₆)		AH ₁₈ (2) (DMSO-d ₆)		
Carbon	Unit A	Unit B	Unit C and C'		Unit D
2,2'	167.82	167.46	167.96	167.68	167.64
3,3'	113.11	108.60	112.81	112.81	109.30
4,4'	177.81	176.35	177.87	177.79	175.81
5,5'	77.96	108.79	77.09	76.87	108.64
6,6'	68.87	149.58	68.64	68.56	147.84
7,7'	73.19	154.40	73.14	73.04	154.93
8,8'	64.17	99.89	64.10	64.01	104.02
9,9'	159.40	154.40	159.72	159.25	151.82
10,10'	124.72	121.81	121.75	121.61	116.90
1"	139.59	139.83	139.66	139.72	139.93
2",6"	128.19	128.19	127.92	127.92	127.92
3",5"	127.88	127.88	127.69	127.69	127.69
4"	126.06	126.06	125.87	125.87	125.74
7"	31.45	31.74	31.30	31.45	31.85
8"	34.16	34.52	33.78	33.95	34.75

a) Assignments of C_5 - C_8 were established by ^1H - ^{13}C shift-correlated spectrum.

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