used in the preparation of tri-(2-methyl-3-thienyl)-phosphine [1] a fraction with b.p. 50—65°/0.15 mmHg (14.5 g) was obtained. Refractionation gave pure (I) as an almost colourless liquid with b.p. 53—54°/0.2 mmHg, yield 12.4 g (73 % based on excess 2-methyl-3-thienyllithium). On storage at −20° the liquid crystallized. (Found: C 70.11; H 9.14; S 20.76. Calc.: C 70.05; H 9.15; S 20.78).

Z-1-Butylthio-1-pentene-3-yne (*I*). To a solution of 2-methyl-3-thienyllithium, prepared from 34.5 g (0.195 mol) of 2-methyl-3-bromothiophene in 75 ml of anhydrous ether and 128 ml of 1.52 N (0.195 mol) butyllithium at −70°, were added 82 g (0.60 mol) of butylbromide in 100 ml of anhydrous ether at −70°. The cooling bath was allowed to reach room temperature and the reaction mixture stirred overnight. The etheral solution was worked up in the usual way [1] and dried. Fractionation gave pure (I) as an almost colourless liquid with b.p. 48—49°/0.1 mmHg, yield 28.5 g (95 %).

Z-1-Butylthio-2-methyl-1-butene-3-yne (*II*). From 0.14 mol excess of 4-methyl-3-thienyllithium used in the preparation of tri-(4-methyl-3-thienyl)-phosphine [1] a fraction with b.p. 42—44°/0.1 mmHg of almost pure (II) was obtained; yield 5.6 g (26 % based on excess 2-methyl-3-thienyllithium). Preparative thin-layer chromatography (silica gel, 5 % ether in petroleum ether) gave (II) in a pure state as a slightly coloured liquid, which should be stored at −20°. (Found: C 69.31; H 9.12; S 20.57. Calc.: C 70.05; H 9.15; S 20.78).

Z-2-Butylthio-2-pentene-4-yne (*III*). From 0.10 mol excess of 5-methyl-3-thienyllithium used in the preparation of tri-(5-methyl-3-thienyl)-phosphine [1] a light yellow fraction with b.p. 42—44°/0.1 mmHg of almost pure (III) was obtained; yield 2.3 g (15 % based on excess 5-methyl-3-thienyllithium). Preparative thin-layer chromatography (silica gel, 5 % ether in petroleum ether) gave (III) in a pure state as a slightly coloured liquid, which should be stored at −20°. (Found: C 70.01; H 9.12; S 20.42. Calc: C 70.05; H 9.15; S 20.78).

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Flavonoids of *Lotus* L.

III.* Mass Spectrometric Detection of 6- and 8-Methoxy Groups in Flavonols

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During the investigation of flavonoids from *Lotus corniculatus* L. a series of new glycosides, derived from 8-methoxy-kaempferol (I) and 8-methoxy-quercetin (II), was isolated.[1,2] This paper describes a method for the detection of 6- and 8-methoxy groups in flavonols based on the mass spectra of I, II, and the related flavonols III to X (Table 1).

Flavonols usually have the molecular ion peak as base peak.[1,3] In the case of I and II, however, the base peak is due to the M−15 ion. Bowie and Cameron [4] ascribe to a *p*-quinoid structure *b* of the abundant M−15 fragments in the mass spectra of 6-*O*-methylated quercetagetin derivatives. By analogy with this we propose the *o*-quinoid structure *a* for the M−15 ions, observed as intensive peaks in the mass spectra of the 8-methoxy-flavonols I to VI.

According to our results an abundant M−15 peak in the mass spectrum of a flavonol is not necessarily indicative of a

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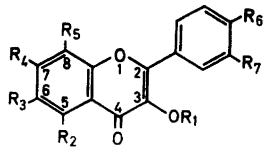
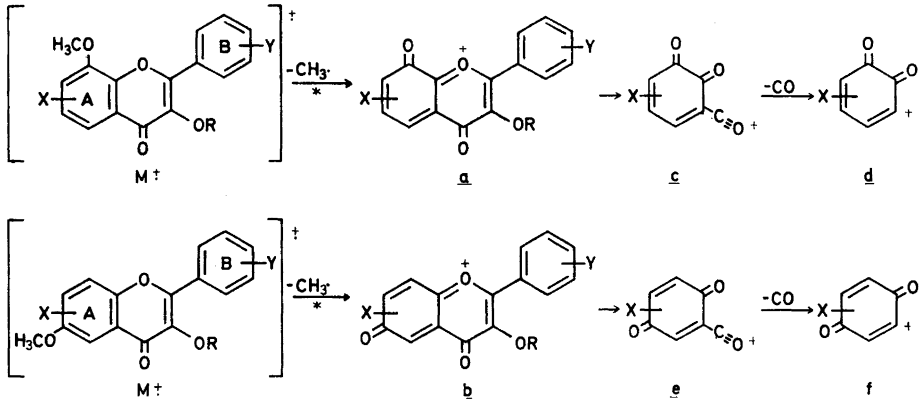
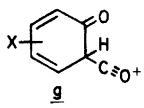


Table 1.

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	M^+		$(M-15)^+$		c or e		d or f	
								m/e	%	*m/e*	%	*m/e*	%	*m/e*	%
I	H	OH	H	OH	OMe	OH	H	316	64	301	100	167	8	139	20
II	H	OH	H	OH	OMe	OH	OH	332	65	317	100	167	4	139	13
III	H	OMe	H	OMe	OMe	OMe	OMe	388	100	373	27	195	7	167	17
IV	D	OMe	H	OMe	OMe	OMe	OMe	389	100	374	33	195	7	167	14
V	Me	OMe	H	OMe	OMe	OMe	OMe	402	100	387	64	195	8	167	14
VI	Et	OMe	H	OMe	OMe	OMe	OMe	416	100	401	66	195	11	167	11
VII	H	OH	OMe	OH	H	OH	OH	332	100	317	17	167	3	139	4
VIII	Me	OMe	OMe	OMe	H	OMe	OMe	402	71	387	100	195	10	167	15
IX	Me	OMe	H	OMe	H	OMe	H	342	67	327	29	—	—	—	—
X	Me	OMe	H	OMe	H	OMe	OMe	372	100	357	66	—	—	—	—





X symbolizes substituents in the A-ring
Y symbolizes substituents in the B-ring
R=H, Me or Et

g

6- or 8-methoxy group. Thus in the spectra of the permethylated derivatives IX and X of kaempferol and quercetin the M−15 peaks are 29 and 66 % of the base peaks, $(M-1)^+$ and M^+, respectively.

We now propose, that the presence of ions with the structures formally depicted as the quinoid species *c* and *d* or *e* and *f* (together with the intensive M−15 ions) is characteristic of 8- and 6-methoxylated flavonols, respectively. These ions, being A-ring fragments, and probably derived from *a* or *b*, are consistently found in the mass spectra of the 8- and 6-methoxylated flavonols, which have been examined (I to VIII). Their composition has been established by exact mass measurements.

Flavonols without 6- and 8-alkoxy groups do not give rise to ions with a composition corresponding to *c*, *d*, *e*, or *f*. Instead, Audier,[5] in an investigation of some flavonols, lacking alkoxy groups in the 8- and 6-positions, found another characteristic A-ring fragment, for which he proposed the structure *g*. This ion contains hydrogen originating from the 3-hydroxy group. In agreement with the formulation of *c* and *d* these ions did not change their masses by deuteration of the 3-hydroxy group in III (*cf.* Table 1).

It is noteworthy, that the base peak in the mass spectrum of 8-methoxyquercetin (II) is due to the M−15 ion, whereas in the spectrum of 6-methoxyquercetin (VII) it is due to the molecular ion. The opposite holds true for the permethylated derivatives of II and VII, which show M^+ and (M^+-15), respectively, as the most abundant ions.

Experimental. The mass spectra were determined by direct insertion technique with an A.E.I. MS902 mass spectrometer, operating at 70 eV and a source temperature of 200 to 250°.

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A Useful Method for Structure Determination of 3,3′-Bithienyls by PMR. II*

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In 2- and 3-carbomethoxythiophenes and in 5,5′-dicarbomethoxy-3,3′-bithienyls, the OCH_3-resonance occurs within the small interval of 6.10−6.20 τ (CS_2) but is shifted 0.2−0.3 ppm upfield when the carboxylic ester groups are situated at the 2,2′- or 4,4′-positions.[1] Various reasons for this were discussed, and although the observed shifts exhibited by the OCH_3 protons of carbomethoxy groups in the positions *ortho* to the pivot bond could be explained in terms of anisotropy effects from the aromatic rings, it could not be excluded that two carboxylic ester groups in a symmetrically substituted 3,3′-bithienyl might shield each other, or that another *ortho* substituent might affect the conformation of the carbomethoxy group relative to the bithienyl skeleton, and thus cause a shift of the OCH_3 protons.

In connection with other work on 3,3′-bithienyls some 3,3′-bithienylmonocarboxylic acid were prepared together with their methyl esters.[2,3] The latter were investigated by PMR and the shifts of the OCH_3 protons are collected in Table 1 together with the τ_{OCH_3}-values of some dicarbomethoxy compounds of interest for comparison.

The data in Table 1 show that even in unsymmetrically substitued 3,3′-bithienyls with only one carbomethoxy group in the molecule at the 2- or 4-position, the OCH_3-resonance is shifted upfield to about the same extent as in symmetrically substituted 2,2′- or 4,4′-dicarbomethoxy-3,3′-bithienyls. This decreases the plausibility of the suggestion that the shift might arise from the mutual shielding of two carbomethoxy groups, and makes it unlikely that the main part of the upfield shift is caused by shielding of other *ortho* substituents since in that case the shift would be more sensitive to the nature of such substituents.

* For Part I see Ref. 1.